

ABSTRACT

BROMFIELD LEE, DEBORAH CHRISTINA DEIRDRE. Development of Sensorial Experiments and their Implementation into Undergraduate Laboratories. (Under the direction of Maria T. Oliver-Hoyo).

“Visualization” of chemical phenomena often has been limited in the teaching laboratories to the sense of sight. We have developed chemistry experiments that rely on senses other than eyesight to investigate chemical concepts, make quantitative determinations, and familiarize students with chemical techniques traditionally designed using only eyesight. Multi-sensory learning can benefit *all* students by actively engaging them in learning through stimulation or an alternative way of experiencing a concept or ideas. Perception of events or concepts usually depends on the information from the different sensory systems combined. The use of multi-sensory learning can take advantage of all the senses to reinforce learning as each sense builds toward a more complete experience of scientific data. Research has shown that multi-sensory representations of scientific phenomena is a valuable tool for enhancing understanding of chemistry as well as displacing misconceptions through experience. Multi-sensory experiences have also been shown to enrich memory performance. There are few experiments published which utilize multiple senses in the teaching laboratory.

The sensorial experiments chosen were conceptually similar to experiments currently performed in undergraduate laboratories; however students collect different types of data using multi-sensory observations. The experiments themselves were developed by using chemicals that would provide different sensory changes or capitalizing on sensory observations that were typically overlooked or ignored and obtain similar and precise results as in traditional experiments. Minimizing hazards and using safe practices are especially essential in these experiments as students utilize senses traditionally not allowed to be used in the laboratories. These sensorial experiments utilize typical equipment found in the teaching laboratories as well as inexpensive chemicals in order

to aid implementation. All experiments are rigorously tested for accuracy and all chemicals examined for safety prior to implementation.

The pedagogical objectives were established of to provide the ability to develop and stimulate students' conceptual understanding. The educational assessments of these experiments are are fashioned using the framework chosen (Marzano and Kendall). All the experiments are designed as collaborative, inquiry-based experiments in aims of enhancing the students understanding of the subject and promote critical thinking skills. These experiments use an investigative approach rather than verification methods. Terminology and misconceptions of the experiment were evaluated to prevent misunderstanding or confusion during the experiment. Interventions to address these misconceptions and learning problems associated with the experiment were developed. We have developed the Learning Lab Report, LLR, as an alternative model for the traditional laboratory reports, with the goal of transforming the traditional reports into something more useful for *both* students and instructors. The educational strategies are employed to develop this format in order to promote students to think critically about the concepts and take an active involvement in learning. From the results of the LLR, all experiments were reviewed and re-written to address any learning problems.

The sensorial experiments study several topics usually covered in the first 2 years of the chemistry curriculum (general and organic chemistry courses). The experiments implemented, organic qualitative analysis, esterification kinetics, Le Chatelier equilibrium, thermometric titrations and ASA kinetics, worked effectively as students were able to draw correct conclusions about the concepts from the data obtained. An olfactory titration using the smell of the rutabaga vegetable has been developed and thoroughly tested. The LLR was utilized with the equilibrium, titration and acetyl salicylic acid experiments. The details of the development, implementation of these sensorial experiments and the LLR and student results are discussed.

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Development of Sensorial Experiments and their Implementation into
Undergraduate Laboratories

by
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DEDICATION

To the loves in my life and my inspiration, my dearest husband, my parents and siblings.

Donjuma, Audré, Charles, Stephanie and Charles Jr.

Truly the wind beneath my wings.

BIOGRAPHY

Deborah Christina Bromfield was born to Audré and Charles Bromfield on June 19th, 1981 in Kingston, Jamaica. She was later blessed with a sister and brother, whom she would eventually grow to love dearly. Her parents worked hard to send the children to Hillel Academy. Deborah did well and even skipped the 5th grade, passing her Common Entrance examinations placing her in one of the premier high school (7th grade, British school system) in the Caribbean. She began high school in 1992 at Immaculate Conception High. Deborah was always a shy but curious child, often investigating things that may not need investigation and once resulted in a broken arm. She had always loved science and wanted to be a pathologist. She loved and excelled in math, physics, religious studies and home economics, and later a new chemistry teacher and her mother's high school friend sparked a passion for chemistry in Deborah. Several major surgeries and CXC exams later, she graduated in 1997, continuing on to the A' levels (British post-secondary examination).

She entered college in 1999 at the University of South Florida and majored in chemistry at which she excelled. She graduated in 2002 and decided to pursue a graduate degree. Still uncertain of what she was going to do next, she found two new loves during graduate school— education (her future in chemistry) and Don Lee (her future husband). She obtained a Master's degree with a research emphasis in Organic Synthesis at Florida Atlantic University under the direction of Dr. Salvatore Lepore. Deborah decided that she wanted to continue in academia and a doctoral degree in a chemical education was her next step. One week after marrying Don in 2005, she moved to North Carolina to join the department of chemistry at NCSU and began research under the direction of Dr. Maria Oliver-Hoyo. Even though, she is not sure what lies ahead of her, she knows with what her parents have instilled in her and what she has learned over the years, she will do great things in her career!

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TABLE OF CONTENTS

LIST OF TABLES.....	viii
LIST OF FIGURES.....	xiv
LIST OF SCHEMES.....	xvi
LIST OF GRAPHS.....	xvii
LIST OF EQUATIONS.....	xviii
LIST OF ABBREVIATIONS.....	xix
CHAPTER 1 . Overview & Proposal.....	1
1.1 Introduction.....	1
1.2 Literature Review.....	2
1.3 Sensory Process Overview.....	5
1.4 Sensory learning.....	26
1.5 Proposal.....	29
REFERENCES.....	31
CHAPTER 2 . Project overview.....	38
2.1 Chemical and pedagogical considerations.....	38
2.2 Educational framework, objectives and assessments.....	43
REFERENCES.....	67
CHAPTER 3 . The Sensorial Experiments.....	70
3.1 The Sensorial Experiments.....	70
3.2 Qualitative Organic Analysis Experiment.....	72
3.3 Esterification Kinetics Experiments.....	84
3.4 Equilibrium Experiments.....	103
3.4 Acetyl salicylic acid kinetics.....	132

3.5 Thermometric Titration Experiments	150
3.6 Olfactory Titration	191
REFERENCES	204
CHAPTER 4 . Conclusions and Future Work.....	217
4.1 Summary and Conclusions	217
4.2 Sensory adaptations	224
APPENDICES	234
Appendix A . Publications.....	236
Appendix B . Qualitative Organic Analysis Experiment.....	244
Appendix C . Esterification Kinetics Experiment	264
Appendix D . Le Chatelier's and equilibrium study	277
Appendix E . Acetyl salicylic Acid Kinetics Experiment.....	305
Appendix F . Thermometric Titrations	325
Appendix G . Olfactory Acid-Base Titrations.....	352

LIST OF TABLES

Table 1.1.	Methods and types of analysis for studying the relationships in the perceptual process.....	7
Table 1.2.	Sound intensities and dangerous exposure times.	13
Table 1.3.	Degree of hearing loss and the decibel ranges.	14
Table 1.4.	Channels and mechanoreceptive fibers associated with receptors.....	15
Table 1.5.	Two point threshold values for various areas on the body.....	17
Table 1.6.	Primary odorants and examples described by Amoore.....	20
Table 1.7.	Some primary odorants and examples described by Jennings-White.....	22
Table 1.8.	Comparison of the odor thresholds for some common chemicals.	24
Table 1.9.	Examples of enantiomers showing differing aromas.	25
Table 2.1.	Description of taxonomy levels of M&K and students' mental operations relative to knowledge domains expressed as educational objectives.	46
Table 2.2.	Example of mental operations acting on the three knowledge domains as it relates to thermometric titrations.....	49
Table 2.3.	Definitions of cognitive and affective Bloom's domains and corresponding levels.	51
Table 2.4.	Comparison of the taxonomies of M&K and Bloom.	53
Table 2.5.	Summary of the problems with Bloom's taxonomy addressed by M&K.	54
Table 2.6.	Basic structure of the Learning Lab Report.	60
Table 3.1.	Reported aroma descriptions and aromas observed in the laboratory.....	75
Table 3.2.	Some odor characterizations made by students.	79
Table 3.3.	Number and percentage of students with problems with olfactory observation or students who did not follow the directions.	79

Table 3.4.	Students' results for three confirmatory tests.....	82
Table 3.5.	Reported aroma descriptions and observed aromas from ester synthesized in the research laboratory prior to use in the kinetics studies.	87
Table 3.6.	Representative values for odor thresholds and volatilities for selected esters.	89
Table 3.7.	Average results obtained when assessing the rate of esterification reactions performed in the research laboratory.	91
Table 3.8.	Average results when evaluating the factors affecting the rate of esterification in the research laboratory. Each data point had a deviation of ± 2 seconds and $n=6$ trials..	92
Table 3.9.	Percentages of student responses characterized by correctness and completeness (C&C), correct but not complete (C) or did not answer the question correctly or completely (N).	95
Table 3.10.	Students' descriptions of observed aromas for Part A.	98
Table 3.11.	Sample data from students on effects of alcohols for Part B.	99
Table 3.12.	Sample data for ethyl acetate aroma detection by varying the amount of (a) ethanol, (b) catalyst and concentration of acetic acid (c).....	100
Table 3.13.	Percentage of student post-lab responses characterized by correctness and completeness (C&C), correct by not complete (C) or did not answer the question correctly or completely (N).....	101
Table 3.14.	ΔH values for the equilibrium reactions.....	106
Table 3.15.	Sample data for complex ion equilibria that rely on color, clarity, sound and temperature changes.....	107
Table 3.16.	Equilibrium that rely primarily on aroma and color changes.....	109
Table 3.17.	Equilibrium with temperature dependence that rely on clarity, sound and temperature changes.....	110

Table 3.18.	Solubility and chromate equilibria reactions that rely on clarity, sound and temperature changes.....	111
Table 3.19.	Equilibrium LLR pedagogical objectives and assessments.	113
Table 3.20.	Percentages of student responses characterized by correctness and completeness.	130
Table 3.21.	Percentages of student responses with thoughtful responses to various questions.	131
Table 3.22.	Problems observed during implementation and interventions to address these.	132
Table 3.23.	Effect of HCl concentration on the time for the emergence of the AcOH aroma (3 trials each).	135
Table 3.24.	ASA kinetics LLR objectives, assessment and associated cognitive skills.	137
Table 3.25.	Change in correctness of kinetics responses for pre-lab questions through reflection.	148
Table 3.26.	Comparison of colorimetric and thermometric titration data using 10.0 mL NaOH.	160
Table 3.27.	Thermometric titration data obtained from the first student volunteer for four acids.	160
Table 3.28.	The experimental and calculated values for the heat capacity of the medium (c_m).	161
Table 3.29.	Density (dependent on the concentration) for ~ 0.5 – 1.6 M HCl, NaOH, NaCl.	162
Table 3.30.	ΔH_n data for traditional and thermometric titration experiments at various concentrations.	163
Table 3.31.	ΔH_d values at infinite dilution for various concentrations of HCl.	163
Table 3.32.	Comparison of data for various ~ 1M acids.	164
Table 3.33.	Titration LLR pedagogical objectives and assessments.	164
Table 3.34.	Observations by touch through test tubes and Styrofoam and temperature changes.	179

Table 3.35.	Percentages of student responses characterized by correctness and completeness.	180
Table 3.36.	Percentage of thoughtful responses related to the demonstration.	182
Table 3.37.	Percentages of student responses characterized by correctness and completeness for similar questions used in both implementations.	185
Table 3.38.	Score changes for pre-lab questions after reflection.	188
Table 3.39.	Problems observed during the implementations with relevant suggestions and modifications.	189
Table 3.40.	Titration using the rutabaga indicator (Method A) compared to various indicators.	201
Table 3.41.	Titration of NaOH vs. HCl using the rutabaga indicator (Methods A-C) compared to standardized concentration using phenolphthalein. * Color change observed.	202
Table 3.42.	Redox indicators (n=3 trials) compared against the rutabaga indicator (CAN vs. Fe ²⁺ and H ₂ O ₂) using method D.	203
Table B.1.	List of Organic Samples/Functional Group and Corresponding Numbers/Letters.	255
Table B.2.	List of Unknowns.	255
Table B.3.	Examples of descriptive words to be used describe the smells of the samples.	256
Table B.4.	All student responses aroma classifications.	256
Table B.5.	Rubric for qualitative organic experiment (Section 203).	261
Table B.6.	Rubric for qualitative organic experiment (Sections 202, 204 and 206).	262
Table B.7.	Grade percentage ranges with the percentage of total student, male (m) and female (f) by lab section.	262
Table B.8.	Number of students with complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N) and average percentages for pre and post lab questions.	263

Table C.1.	Amount of carboxylic acid needed to make solutions with various concentrations.	268
Table C.2.	Sample data for students' results for Table 2.....	271
Table C.3.	Example of the variability of results of two groups of students.....	271
Table C.4.	Sample of volume equivalents for reagents drops used in Part B.....	272
Table C.5.	Number of students responses by correctness as percentages for esterification pre and post lab questions.	276
Table D.1.	Chemicals and quantities needed for equilibrium experiment.....	298
Table D.2.	Number of students with complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N) in the equilibrium pre-lab questions.	302
Table D.3.	Complete chloride source investigation data.	303
Table D.4.	Common drying agents' strength and power of dehydration.....	304
Table E.1.	Number of students with complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N) in the ASA kinetics titration pre- lab questions.....	321
Table E.2.	Rubric and percentage of FS students with C&C, C, SC and N responses.....	322
Table E.3.	Percentage of first semester students with C&C, C, SC and N responses (section of lab separated and graded based on correctness).....	323
Table E.4.	Rubric and Percentage of second semester students with C&C, C, SC and N responses.	323
Table E.5.	Average and medium scores for SS section for the entire lab grade.....	324
Table E.6.	Concentration of acetic acid in air around experimental set-up.....	324
Table F.1.	Concentrations and quantity of titration solutions needed.....	344

Table F.2.	Number of students with complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N) in the titration pre-lab questions.	349
Table F.3.	Average for each titration question of the pre-lab prior to and after the experiment.	350
Table F.4.	Percentage of complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N).	350
Table F.5.	Sample observations of the dilution of H ₂ SO ₄	351
Table F.6.	Observation of temperature changes of dissolution reactions.....	351

LIST OF FIGURES

Figure 1.1.	Perceptual cycle with an example of the visual perceptual process of an apple.	5
Figure 1.2.	Electrical activity in axon.	9
Figure 1.3.	Spectral sensitivity curves of visual pigments in cones.	11
Figure 1.4.	Audibility curve.	13
Figure 1.5.	Response of warm and cold fibers to temperature stimulus.	16
Figure 1.6.	Locations of the receptive field centers for various skin mechanoreceptors.	17
Figure 1.7.	Some exploratory procedures.	18
Figure 1.8.	Proposed olfactory receptor sites with representative compounds proposed to fit them.	21
Figure 2.1.	The M&K's systems of thought levels and domains of knowledge.	44
Figure 3.1.	Lumitest light probe.	76
Figure 3.2.	Sample calculations to approximate concentration of esters in air for the ethyl and propyl acetate (ppm).	90
Figure 3.3.	Esterification experimental set-up.	93
Figure 3.4.	Students' esterification mechanisms.	96
Figure 3.5.	Esterification mechanism with explanations for each step.	97
Figure 3.6.	Kinetics hydrolysis experimental set-up.	137
Figure 3.7.	Section of kinetics post lab question depicting reaction at the molecular level.	140
Figure 3.8.	Calculation diagram for the ASA kinetics.	142
Figure 3.9.	Thermometric titration apparatus.	159
Figure 3.10.	Taber's diagram depicting an acid at different concentrations and strengths.	168
Figure 3.11.	Calculation and conversion diagram.	177
Figure 3.12.	Sample of the C&C response for activity question 1.	181

Figure 3.13.	Sample of the C response to activity question 1 with incorrect water structure.	181
Figure 3.14.	Sample SC response with incorrect structures and charges to activity question 1..	181
Figure 3.15.	Sample of the N response to activity question 1 showing incorrect Lewis structure and an inappropriate response to the question.	181
Figure 3.16.	Sample C&C response for the reversal of the order of addition of reagents.	186
Figure 3.17.	SC diagram for the reversal of the order of addition of reagents.....	186
Figure 3.18.	Incorrect reverse addition diagram.	186
Figure 3.19.	Sample C&C response to post-lab question 5.....	187
Figure 3.20.	Sample N response for pictorial representation of diprotic acid titration	187
Figure 3.21.	Sample pictorial representations of the titration for post-lab question 1.	188
Figure 3.22.	Aglyconic side chains with average content of rutabaga glucosinolates.	192
Figure 3.23.	Generic structure of glucosinolate showing anomeric carbon resembling <i>O,S</i> -acetal.	192
Figure 3.24.	Purin-6-yl-1-thio-D-glucopyranosides (204) and oxathiolanes (209) used to determine hydrolysis mechanism.....	194
Figure 3.25.	Polar effects with attached groups.	195
Figure 3.26.	Resonance effects of leaving group on the hydrolysis mechanism.....	195
Figure 3.27.	ETI talking thermometer.....	229

LIST OF SCHEMES

Scheme 3.1.	Sample chemical tests and expected results for alcohol and carboxylic acid.	76
Scheme 3.2.	Sensorial observations of functional groups with characteristic tests.	81
Scheme 3.3.	Flow chart of the esterification kinetics experimental procedure.	97
Scheme 3.4.	Equilibrium terminology map.	122
Scheme 3.5.	Equilibrium LLR experimental components and design.	128
Scheme 3.6.	Hydrolysis of acetyl salicylic acid produces a vinegar aroma from acetic acid.	133
Scheme 3.7.	Mechanism of ASA acid-catalyzed hydrolysis.	134
Scheme 3.8.	Mechanism of ASA base-promoted hydrolysis.	135
Scheme 3.9.	Potential mechanisms for <i>O,O</i> - or <i>O,S</i> - acetal acid-catalyzed hydrolysis.	193
Scheme 3.10.	Final step of both mechanisms - Lossen like rearrangement to form the isothiocyanate.	196
Scheme 3.11.	Breakdown product of β -hydroxyl isothiocyanate.	196
Scheme 3.12.	Redox reaction using CAN (Ce^{4+}) with Fe^{2+} and H_2O_2	197
Scheme 3.13.	Proposed intermediate for redox titration for indole glucosinolate.	197
Scheme 3.14.	Proposed mechanism for the oxidation of the hydroxyindoles using Fremy's salt.	198
Scheme 3.15.	Oxidation of sulfide side chain to produce sulfinyl groups.	198
Scheme 3.16.	Oxidation of sulfide at the anomeric carbon.	199
Scheme 3.17.	Oxidation of sulfide of <i>s</i> -pyridyl glycoside.	199
Scheme C.1.	Fisher Esterification Mechanism	269
Scheme G.1.	Proposed complete mechanism depicting C-S cleavage of glucosinolate.	362
Scheme G.2.	Proposed complete mechanism depicting C-O cleavage of glucosinolate.	362

LIST OF GRAPHS

Graph 3.1	Distribution of students' grades as the probability of z-scores (Normative data).....	83
Graph 3.2.	Graph depicting disturbances (A-D) in the complex ion equilibrium.....	116
Graph 3.3.	Representative pre-lab activity concentration vs. interval/time graph.....	117
Graph 3.4.	Representative graph of $\ln[\text{ASA}]$ vs. time.	136
Graph 3.5.	Representative graph of $[\text{ASA}]$ vs. time.	136
Graph 3.6.	Representative graph of $1/[\text{ASA}]$ vs. time.	136
Graph 3.7.	Enthalpimetric graph for the traditional determination of ΔH	151
Graph 3.8.	Representative thermograms for (a) an ideal titration and (b) actual titration results.	153
Graph 3.9.	Temperature effect on graph due to the titrant and analyte.....	155
Graph 3.10.	Determination of ΔH_n using Method A.....	156
Graph 3.11.	Determination of ΔH_n using Method B.....	157
Graph 3.12.	Graph of temperature vs. time for calibration of the Styrofoam cups to determine c_m	161
Graph 3.13.	Thermometric titration graph for NaOH vs. HCl.....	183
Graph 3.14.	Student thermometric graph using Method A.....	183
Graph 3.15.	Student thermometric graph using Method B.	184

LIST OF EQUATIONS

Equation 1.1.	Weber's Law.....	7
Equation 3.1.	Typical calorimetric equation.....	152
Equation 3.2.	Energy and enthalpy equation.....	152
Equation 3.3.	Temperature change equation.....	152
Equation 3.4.	Derivation of calorimetric equations.....	153
Equation 3.5.	Equation for the slope of the thermogram.....	153
Equation 3.6.	Equation to determine enthalpy.....	153
Equation 3.7.	Approximation of c_t	154
Equation 3.8.	Total heat capacity of system.....	154
Equation 3.9.	Resulting enthalpy equation.....	154
Equation 3.10.	Enthalpy equation for medium.....	154
Equation 3.11.	Determination of heat capacity of medium.....	154
Equation F.1.	Heat of cooling (mix hot + cold).....	351
Equation F.2.	Heat lost by hot water.....	351
Equation F.3.	Heat gained by cold water.....	351
Equation F.4.	Heat lost or gain in insulators.....	351
Equation F.5.	Heat of calorimeter.....	351
Equation F.6.	Resulting calorimetric equation.....	351

LIST OF ABBREVIATIONS

ASA	acetyl salicylic acid
C	Correct but not complete response
C&C	Complete and correct response
c_a	Heat capacity of container, J/K
c_m	Heat capacity of the medium, J/K
CNS	Central nervous system
c_s	Specific heat capacity (intensive property), J/gK or J/g°C
c_t	Total heat capacity (extensive property), J/K or J/°C
c_w	Specific heat capacity of water, intensive property , 4.18J/gK
ΔH_d	enthalpy of dilution, J/mol
ΔH_n	enthalpy of neutralization, J/mol
ΔH_s	enthalpy of solution, J/mol
ΔT	change in temperature $T_F - T_I$, K or °C
EDG	electron donating group
EP	exploratory procedures
Et	ethyl
EtOH	ethanol
EWG	electron withdrawing group
FG	functional group
fMRI	functional magnetic resonance imaging
FS	First semester
FTIR	Fourier transform infrared spectroscopy

FV	First student volunteer
GC-MS	gas chromatography-mass spectroscopy
GLC	gas-liquid chromatography
GS	Glucosinolate
i-pr	isopropyl
IR	infrared spectroscopy
K_{eq}	thermodynamic equilibrium constant
k_f	forward rate constant
k_r	reverse rate constant
LCP	Le Chatelier's principle
LED	light-emitting diode
LLR	Learning Lab Report
lp	light probe
m	slope of a line
M&K	Marzano and Kendall
Me	methyl
MeOH	methanol
MORE	Model–Observe–Reflect–Explain
MSDS	Material Safety Data Sheets
M_t	Molarity of titrant, M
N	Incorrect and incomplete response
NMR	nuclear magnetic resonance
n_p	moles of product

NP	non-Pacinian
p	pressure of stimulus
PET	positron emission tomography
PNS	Peripheral nervous system
ppt	precipitate
Pr	propyl
q	amount of heat
Q_c	reaction quotient
R	<i>rectus</i> for right, enantiomer stereochemistry
S	<i>sinister</i> for left, enantiomer stereochemistry
SC	Somewhat correct response
sol'n	solution
SS	Second semester
SV	Second student volunteer
SWH	Science Writing Heuristic
T or temp	Temperature, K or °C
TA	teaching assistant
<i>t</i> -bu	tert-butyl group
V_t	Volume of titrant, L

CHAPTER 1 . Overview & Proposal

1.1 Introduction

Even though chemistry involves the investigation of everything we experience through all our senses, “visualization” of chemical phenomena often has been limited in the teaching laboratories to the sense of sight traditionally. We have developed sensorial chemistry experiments to investigate chemical concepts, make quantitative determinations, and familiarize students with chemical techniques traditionally requiring only eyesight. These sensorial experiments were designed to utilize multiple or different senses in making chemical determinations. The research objectives of this dissertation project are both scientific (chemical) and pedagogical in nature. In order to develop sensorial experiments, a strong knowledge of chemical principles and reactions must be learned and utilized. In these experiments, the chemistry is manipulated in order for the students to explore reactions and principles with senses other than eyesight. The chemistry of the experiments is thoroughly screened so that students may perform the experiments in a safe manner, as they will be relying on senses traditionally not employed in the teaching environment. These sensorial experiments utilize typical equipment found in teaching laboratories as well as inexpensive chemicals in order to aid in their implementation.

In addition to this unique multi-sensory dimension of the experiments, a novel laboratory format was developed to promote a valuable learning opportunity from these experiments which allows students to creatively explore these reactions through a structured writing format. We have developed the Learning Lab Report, LLR, as an alternative model for the traditional laboratory report, with the goal of transforming the laboratory reports into something more useful for *both* students and instructors. A variety of educational strategies were employed to develop this format in order to promote students to think critically about the concepts and take an active involvement in

their learning. The format also allowed *instructors* to monitor students' thought processes from the pre-lab to post lab, thereby aiding pedagogical modifications of the experiments. In addition to this new format, all the experiments were designed as collaborative, inquiry-based experiments that used an investigative approach rather than a verification one in aims of enhancing the students understanding of the subject and promoting critical thinking skills. The experiments study several topics usually covered in the first 2 years of the chemistry curriculum (general and organic chemistry courses). The literature review, proposal, pedagogical framework, novel laboratory format and development and results of these experiments are presented.

1.2 Literature Review

There are few experiments published which utilize different senses to perform chemical experimentation in teaching laboratories. Some of these experiments have used the sense of smell such as in the case of olfactory titrations. Wood and Eddy demonstrated the use of the odor of raw onions as an endpoint indicator in acid-base titrations and compared the endpoints to the titrations performed using phenolphthalein (1). Onion and garlic were used by Neppel et al. as indicators in olfactory titrations to determine endpoints. The manipulation of pH conditions allowed garlic to be used as an olfactory indicator through the breakdown of aliin to sulfur compounds that produce the characteristic garlic aroma (2). The aroma of the raw garlic is perceived under neutral or acidic conditions, while no aroma is present under basic conditions. Eugenol, thymol, vanillin and thiophenol were tested by Flair and Setzer as olfactory indicators with eugenol showing potential for use in back-titrations (3). Rancke-Madsen and Krogh used smell in determining the end point in a strong acid/base titration using sodium butyrate, sodium sulfide, quinoline, pyridine, and ammonium chloride (4), showing their use as accurate olfactory indicators. An innovative approach by Anderson and Buckley consists of an interactive demonstration that explores K_{eq} and acid-base properties using

the sense of smell (5). In the demonstration students rank the degree of the ammonia observed from the reaction of ammonium chloride with different bases of varying strengths, demonstrating that the acid-base reaction that had the strongest smell has the largest K_{eq} .

Hiemenz and Pfeiffer described conductivity titrations of NaOH with trichloroacetic acid where the endpoint is detected audibly using a modified conductivity cell and balance (6). The experiment involves production of a continuous sound through an amplifier, which is nullified at the endpoint, and the tarred sample is re-weighed to determine the amount of base added. A modified Beckman Zeromatic II pH meter with an audio-encoded Simpson meter was used by Tallman to perform acid base titrations (7). This experiment was performed successfully by the first blind student at North Dakota State University who was surprised how well laboratory work supported class work. Ratiff devised conductivity experiments that use sound rather than the traditional LED set-up to determine the conductivity of various solutions using simple materials such as a minibuzzer and a 9V battery (8).

The sense of touch has also been used to explore various science areas such as allowing students to “feel” intermolecular forces and molecules using a variety of haptic equipment. An inexpensive method to measure density using a ruler and weights for measuring displaced water by irregular solids was discussed also by Ratiff (8). Anderson used the Optacon (optical tactile converter) with a photosensitive head capable of perceiving a LED digital display to translate images into vibrations (9). A cost effective tool to aid with the visualization of molecular quantum dynamics utilizing web-based software and haptic technology was described by Davies et al (10). Sato et al have developed a tool to study intermolecular forces, where they were able to recreate Van der Waals and electrostatic forces using SPIDARG devices, which are haptic interface that are manipulated by a grip with 8 strings. (11). Jones et al. explored haptic technology (nanoManipulator) which uses the sense of touch to provide students with the opportunity to explore the microscopic

world (12). The nanoManipulator uses a microcomputer programmed to control a joystick device which gives tangible response from an atomic force microscope (AFM). MolySim is a molecular modeling software being used to help students to visualize molecules by assembling a molecule, displaying its different conformations, and providing the dynamic energetics of the system (13). The program utilizes a novel joystick which allows the student to 'feel' the properties of the molecule.

These few published experiments and sensory equipment that utilize smell, hearing and touch allow students to perceive scientific concepts through senses other than eyesight, demonstrating the usefulness of the senses in making observations. Our sensorial experiments allows for the exploration of chemistry, which explores everything we experience through our senses, with multiple or different senses. The use of multi-sensory experiences can take advantage of all the senses to support learning in the laboratory as each sense builds toward a more complete experience of the chemical concept explored. The development of sensorial experiments provides a resource for the utilization of the senses in the undergraduate chemistry laboratory in a safe way.

In order to develop sensorial experimentation to take advantage of the usefulness of the different senses in making chemical determinations, the ability for the senses to be used in making chemical observations was explored. The five human senses (sight, hear, smell, taste, and touch) are a vital part of our interaction with the outside world as they are the physiological manner of perception. The perceptual process is a chain of events that commences with environmental stimulus (distal), resulting in our perception of a stimulus and an action in response to the stimulus (14) and is basically our sensory experience of the world and our recognition of what we observe. An overview of the perceptual process, sensory processes and sensory thresholds was examined. A summary of the basic mechanisms of senses is presented, however, the sense of taste is excluded as it not a viable method of observation in a chemistry teaching laboratory.

1.3 Sensory Process Overview

Perceptual process

The perceptual process is dynamic, as it is continually changing from one received stimulus to action. Figure 1.1 provides an example of the perceptual process with the cyclical visual perceptual process of viewing an apple. The *distal stimulus* takes place at a distance such as when looking at a stimuli (apple) (14). The distal stimuli can either be environmental or attended stimuli. Environmental stimuli are all the stimuli available to the observer such as the view of an entire classroom. *Attended stimuli* are stimuli that are the point of focus of the observer for example a book on a table in the classroom (15).

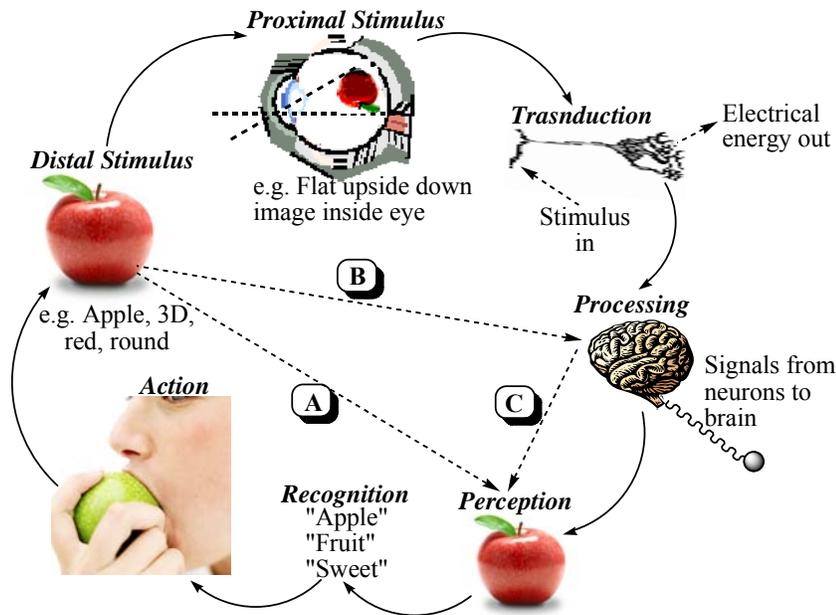


Figure 1.1. Perceptual cycle with an example of the visual perceptual process of an apple.
* Arrows A, B, and C indicate three relationships measured by researchers.

The *proximal stimulus* is that which is in proximity to the sensory receptors such as the image of the apple stimulating the receptors of the eye. Changes that may occur in the creation of the proximal stimulus can have a big impact on perception such as removing eyeglasses significantly

impacts the proximal image resulting in an altered perception, but does not affect the distal stimulus. The proximal stimulus is converted into electrical energy in the transduction stage, which generates electrical signals in the neurons (nerve cells) for neural processing (Figure 1.1). The electrical signals are transferred through the nerves to the brain to be transformed into the perception of the stimulus. The ability for us to categorize the stimulus and give it meaning is the recognition stage and is a different process from perception. Recognition and perception often lead to an active response.

In order to study the perceptual process and understand what people perceive via their senses, scientists use various methods to observe the *stimulus-perception* (A), *stimulus-neural processing* (B) and *neural processing-perception* (C) relationships (Figure 1.1). These relationships in the perceptual process can be analyzed by studying the physiological (or phenomenological) and psychophysical levels shown in Table 1.1 (15,16). The psychophysical method is used to measure the stimuli-perception relationship (A) and involves asking a subject to describe what they perceive. These types of studies are qualitative forms of measurement important in studying the perceptual process showing that various perceptions can alter a person's expectation (14,15).

The *physiological methods* study the relationship between the stimulus and physiology. The stimulus-neural processing relationship (B) is observed by presenting a stimulus and measuring the electrical response of the nervous system. The neural processing-perception relationship (C) is studied using both methods where the physiological and perceptual responses measured the same stimuli (17). The *psychophysical method* involves measuring sensory thresholds (14). Sensory thresholds are the smallest stimuli detectable by the observer, i.e. stimuli that is less intense than the sensory threshold will not elicit sensation (18). Absolute and difference thresholds are two types of sensory thresholds that are studied and are necessary to examine when developing sensorial experiments.

Table 1.1. Methods and types of analysis for studying the relationships in the perceptual process.

	Method	Analysis	Example
A	Psychophysical	Stimulus-perception	Person describing a stimulus.
B	Physiological	Stimulus-neural processing	Monitoring neural firing in response to a given stimulus.
C	Psychophysical and physiological	Neural processing-perception	Observing neural firing and descriptions of a given stimulus.

Absolute threshold is the *minimum intensity* of the stimuli detected 50% of the time by a subject. Gustav Fechner described three methods to measure absolute thresholds: method of constant stimuli, limits, and adjustment (18). The method of constant stimuli measures stimuli of varying intensities presented in random order to a subject and is the most accurate but slowest method. The method of limits occurs when stimuli are presented in ascending or descending order and even though it is the fastest method it is the least accurate. The observer responds when the stimulus is perceived and the cross-over point of the ascending and descending order is the threshold (15). The method of adjustments arises when the stimuli intensity is slowly changed until the observer can barely detect it. This method is done repeatedly to obtain an average (14). The *difference threshold*, described by Ernst Weber, measures the *smallest difference* between two stimuli that a person can detect 50% of the time and is sometimes referred to the just-noticeable difference (18,19). The same methods used to observe the absolute threshold can be used to as observe the difference threshold (15). Weber also observed that despite the magnitude of stimuli, two stimuli must differ by a constant in order for their difference to be detected. This observation led to the formulation of Weber's law shown in Equation 1 (20,21).

$$\frac{\Delta I}{I} = k$$

ΔI - difference threshold
 I - initial stimulus intensity
 k - constant

Equation 1.1. Weber's Law.

The brain and the nervous system

Although the operation of the brain is vastly complex, information is known about the brain and its connection to our sensorial perceptions. The activity of the cerebral cortex is the focus of a significant amount of research as one of its functions is creating perception particularly through modular organization - functional compartments separated from each other or into separate structures (22). The organization of the senses is into primary receiving areas, in which the signals are received in the brain by the sensory receptors. The nervous system is divided into two parts, the central (CNS - spinal cord and brain) and peripheral (PNS - spinal and cranial nerves) nervous systems which communicate and interact with each other. The CNS is responsible for integrating, processing and coordinating sensory data and motor information and is responsible for learning, memory and emotion (23). The PNS conducts sensory information to the CNS (afferent system) and carries motor commands from the CNS (23). Axons are composed of nerve fibers which carry sensory and motor information in the PNS by conducting electrical impulses (action potential). Receptors are sensory structures that detect internal stimuli or respond to external stimuli, while effectors respond to motor information with a reaction from the CNS (23).

The basis of the nervous system is the electrochemical conductance of impulses through axons (neuron). A stimulus disturbs the resting potential of the axon, producing a temporary change in the axon, and consequentially a graded potential which when large enough produces an action potential (23). The action potential is the impulse transmitted along the axon (more positive voltage), and the resting potential (-70mV) returns after the action potential passes down the axon (Figure 1.2) (24). The cell is polarized during the resting conditions and depolarized as the voltage moves across the nerve. The time taken for an action potential to occur is the refractory period.

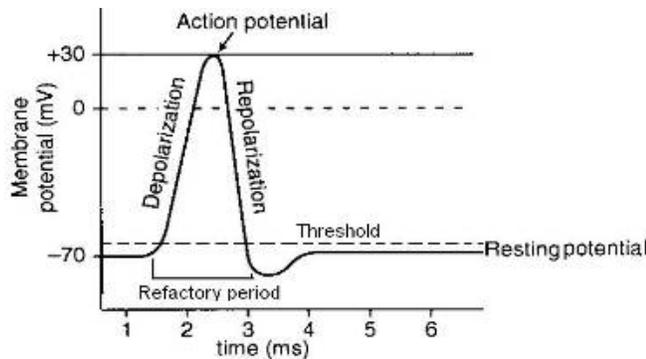


Figure 1.2. Electrical activity in axon.

Our knowledge of the world is limited to the stimuli that excite our sensory receptors. Sensory receptors are the interface between our nervous system and the internal and external environments (23). The senses consist of general (pain, pressure, touch, vibrations, and proprioception) and special senses (vision, gustation, olfaction and hearing). The special senses are more complex and its receptors are located in sense organs, while general sense receptors are distributed throughout the body (23). The visual, auditory and tactile organs detect physical stimuli directly while the olfactory and gustatory organs sense objects through chemoreception processes. In order to understand how humans perceive the world, the basic concepts of sensory receptors and processing are explored.

The sense of sight

Sight (vision) is the ability of the eye in conjunction with the brain to detect electromagnetic waves within the visible range of the electromagnetic spectrum. The light energy that enters the eye occurs typically by light being reflected off an object. The retina contains receptor cells (rods and cones) which synapse (site of communication between nerves) into the neurons. The visual pigments, organic compounds found in the cones and rods, absorb photons and isomerize, which results in the excited receptors generating electrical signals which are transmitted to visual receiving areas (23).

Visual perception has been explained by a variety of theories and experimental data. One obvious quality of vision is the ability to perceive color and our emotional connection to colors. Color is thought to aid perceptual organization (separation of areas) and hence is potentially crucial for survival. Achromatic color (black, white and grey shades) is due to the neural processing in the rods, while chromatic color (all colors excluding white, black and shades of grey) is due to processing in the cones. Our ability to observe color is due to solid objects reflecting certain wavelengths of light and fluid objects transmitting certain wavelengths (14).

Johannes von Kries in 1896 proposed the duplicity theory of vision which states that rods function to aid dark adaptation (how the eye recovers its sensitivity in the dark after exposure to bright light) while spectral sensitivity (color or light sensitivity) is due to the cones (24,26). Rods provide information about the absence or presence of photons, and the cones provide information on the wavelength (23). The increased sensitivity of the receptors during dark adaptation is due to the rate of visual pigment regeneration (27), where the rods are significantly slower (more sensitive in dark) than the cones and more sensitive to shorter wavelengths of light (28). This leads to the Purkinje shift (described by Johannes Evangelista von Purkinje in 1825) which is the inclination for the sensitivity of the eye to shift toward the blue region of the color spectrum (500nm and lower) at low levels of light (29,30).

The spectral sensitivities are due to the differences in light absorption of the cone visual pigments (23). The Young-Helmholtz theory of color-vision hypothesizes that there are three cone receptors, each of which is sensitive to one part of the visible spectrum and any color may be matched by mixing these primary colors (red, green, and blue) and varying their relative signals intensities (30, 31). Wald and Brown used spectrophotometry to measure the wavelengths absorbed by the color vision pigments in the cones and determined the absorbance spectrum of five visual pigments as shown in Figure 1.3 (32). Wald also suggested that the lack of any of these pigments

would lead to certain non-genetic related color-blind disorders. The opponent-process theory of color vision (developed by Ewald Hering) suggests that there are some color combinations that can not be observed, such as red-green or yellow-blue (14,33). The opponent-process theory was shown to be due to the overlap in the wavelengths of these pairs causing an antagonistic effect where opponent cells in the cortex respond positively to one of the color pair while negatively to the other (14).

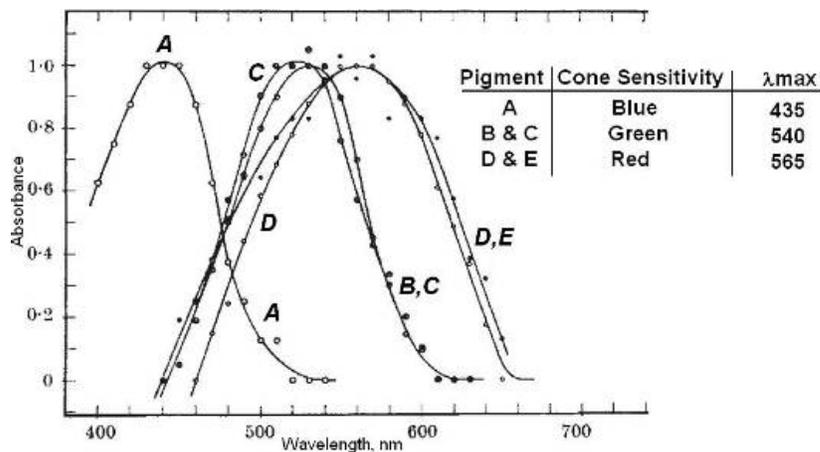


Figure 1.3. Spectral sensitivity curves of visual pigments in cones.

The inability to see is called blindness, which encompasses different degrees of vision loss or other visual impairments. There are different types of visual deficiencies and visual problems where the statistics on the effect of these problems on the population vary for each form of disorder. Some major types of vision problems include genetic disorders, improper focus of light on the retina, damage to the retina and optic nerve damage. Color blindness or deficiencies are conditions that affect the ability to perceive color, and include various categories of dichromatism to monochromatism deficiency. Red-green deficiency (form of dichromatism) is the most familiar form, affecting males (8%, 1 in 12 males) more often than females (<0.4%, 1 in 2500 females) of European ancestry and is due to the inheritance of the gene from the X chromosome (34). Blue-yellow color deficiency affects males and females equally, with the disorder occurring in less than 1 in 10,000 people around the world. Achromatopsia (monochromatism) is the inability to see any

color and affects about 1 in 30,000 people (34). The opponent-process theory has been associated with some of these color deficiency disorders (14). Focusing problems of the eye affect the perception of images and include myopia (near-sighted), hyperopia (farsighted) and astigmatism affecting 30%, 25% and 16.5% of the US population respectively (35). Corrective lens can be used to correct these problems, but require different strengths depending on the severity (37).

The sense of hearing

Hearing is the detection of sound vibrations propagating through a medium such as air. It is the sense of sound perception. Our observation of sound vibrations is not directly observed, but rather the effect of the vibration on the pressure of the medium. Acoustic or sound stimulus is the physical pressure change that takes place allowing for the experience of hearing while changes in pressure of the medium are sound waves (14). Quality of sound is related to the frequency (repetition of cycle per second, Hertz, Hz) and amplitude (height of wave) of a tone. Humans are most sensitive to frequencies in the range of 1,000-4,000Hz, however (38), children and young adults can detect frequencies ranging from 20-20,000Hz (39). The unit of sound is the decibel (dB) and is related to the sound pressure of stimulus (p) and standard sound pressure (p_0 , usually 20 μ Pa) by $dB = 20 \times \log \frac{p}{p_0}$. The threshold (lowest audible sound) is considered to be 0dB at 1,000Hz, (39). The smallest change in air pressure that humans are sensitive to is 10-15dB above air pressure generated by random motion of air molecules.

Various structures of the ear and mechanisms affect the perception and quality of sound such as pitch (perceived frequency of sound) and loudness (magnitude of auditory sensation) (38). Table 1.2 contains sound intensities with corresponding decibel levels and example sounds (23,40). We are more sensitive to certain frequencies than others and the auditory curve is a representation of this. The audibility curve is a graph of the threshold of hearing (intensity) versus frequency, and is used as

the reference level when measuring hearing loss (Figure 1.4) (14,41). The minimum intensity in the threshold of hearing occurs at about 4,000 Hz (39). The audibility curve indicates the sound intensity that creates the same perception of loudness or intensity of sound at various frequencies. The differences in timbre are caused by the relative strength of the harmonics as well as the time from the start to the end of the tone (14).

Table 1.2. Sound intensities and dangerous exposure times.

Decibel Level	Example	Dangerous time exposure
0	Lowest audible sound	
30-50	Soft whisper, quiet library, gentle breeze, refrigerator	
70	Busy traffic, noisy restaurant	Some danger if continuous
90	Shop tools, gas lawn mower, truck noise	Less than 8 hours
100	Chain saw, pneumatic drill, babies' cry	2 hours
120-140	Gun shot, sandblasting, jet plane	Immediate danger
160	Rocket launching pad, shot gun	Hearing loss inevitable

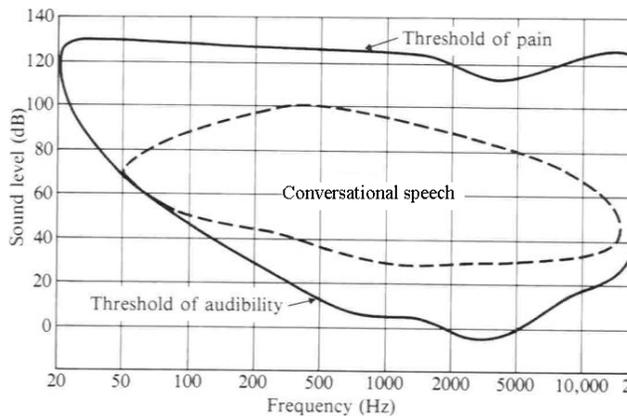


Figure 1.4. Audibility curve.

There are numerous diseases and conditions associated with hearing impairment or deafness (42). Auditory problems may arise due to sound not properly transmitted to the receptors, damaged hair cells, damage to the auditory nerve or auditory cortex or age and these vary in severity. The degree of hearing loss compared to normal hearing is shown in Table 1.3 (43). Approximately 16.1% of Americans experience hearing loss at normal conversational frequency (44). Hearing loss that

results from damage to the outer or middle ear not permitting transmission of vibration occur in 0.8% of the population and are not severe as they often times can be surgically corrected or relieved with hearing aids (45). Damage to the hair cells of the inner ear or nerves results in sensorineural hearing loss (permanent) accounting for 8% of the population (90% of all types of hearing loss) and can range from mild to profound (24,45). For this type of hearing loss, surgery can not correct the loss and often hearing aids do not help as they may amplify sounds but remain unclear.

Table 1.3. Degree of hearing loss and the decibel ranges.

Degree of hearing loss	dB range
Normal Hearing	0-20dB
Mild Hearing Loss	20-40 dB
Moderate Hearing Loss	40-65 dB
Severe Hearing Loss	65-90dB
Profound Hearing Loss	95 and up dB

Persons who are deaf or deaf and blind are able to determine what is being said to them using the vibrations of the person's mouth and face by placing their hand on the speakers face. Tadoma is a tactile speech method where a deaf or deaf/blind person places the thumb on the speaker's lips and other fingers along the jaw line (46). Reed et al. have demonstrated that good speech reception can be achieved through the tactile sense and showed that performance is approximately equal to that of normal listening in noise or babbling with a signal-to-noise ratio of 0-6 dB. Reed used a Tadoma system to monitor and translate signals from the speaker's face into tactile information which then is outputted in to an artificial face. The ability of deaf or deaf and blind students to easily make observations by touch would allow them to actively participate in the undergraduate laboratory with experiments that utilize tactile sensations (Chapter 4).

The sense of touch (Cutaneous Senses)

Touch or somatic sensation generally involves the skin, the heaviest organ in the human body with the largest surface area. Touch can give information about an object that may not easily be

noticeable by sight, such as surface texture. Cutaneous sensations are based on stimulus of skin receptors and allows for tactile (pressure), temperature and pain perception (47). These receptors serve different functions based on the physical properties, location and size of the receptor. These receptors synapse (site of communication between nerves) into mechanoreceptive or thermoreceptive nerve fibers, depending on the function of the receptor. Mechanoreceptive nerve fibers respond to tactile frequency changes or mechanical displacement, while thermoreceptive fibers respond to temperature changes. The nerve fibers allow signals to proceed to the somatosensory receiving area in the parietal lobe and the secondary somatosensory cortex (14,23).

Mechanoreceptors are classified as tactile receptors, baroreceptors, and proprioceptors. The tactile receptors provide sensation of touch, pressure and vibration. The baroreceptors detect pressure changes in blood vessels, digestive, reproductive and urinary tracts. The proprioceptors monitor positions of joints and muscle (23). Tactile sensations are felt by the displacement of skin, and the sensation occurs via separate receptor channels, which are described by the four different receptors that are sensitive to different stimuli at different frequency ranges (Table 1.4). Four types of mechanoreceptive fibers associated with tactile receptors are classified as either rapidly adapting (RA I and Pacinian, P) or slowly adapting (SA I and SA II).

Table 1.4. Channels and mechanoreceptive fibers associated with receptors.

Receptor	Channel	Frequency	Fiber	Stimulus	Perception
Merkel	NP III	0.3-3Hz	SA I	Pressure	Pressure
Meissner	NP I	3-40Hz	RA I	Taps	Flutter
Ruffini	NP II	15-400Hz	SA II	Stretching	Buzzing
Pacinian	PC	10>500Hz	P	Rapid vibration	Vibration

Warm and cold sensations are felt by separate thermoreceptors (warm and cold fibers). These thermoreceptors are located in the dermis in skeletal muscle, liver, and in the hypothalamus (23). Cold fibers respond increasingly to a decrease in temperature between 20-45°C and are three or four times more numerous than warm receptors (14,23). The warm fibers respond more to increasing

temperature between 30-48°C (Figure 1.5) (24). Extreme temperatures in either direction cause pain (14,48). Thermoreceptors are very active when temperature changes, however adapts quickly to stable temperatures (23). Temperature sensations take place along the same pathways as pain sensations (23). Nociceptors respond to intense stimulations such as severe temperatures and immense pressure. Pain perception is affected by an individual's culture and past experiences. Sarlani et al have shown that women tend to report greater sensitivity and perceived unpleasantness to experimentally induced thermal pain at 15°C and 44°C than males, but showed no significant difference in thermal sensitivity and adaptation to temperatures between 15°C and 44°C for both genders (49). This research also showed no difference in thermal intensity for both sides of the body (equal laterality) but lower thermal threshold was noted with the left hand vs. the right hand. Functional magnetic resonance imagining (fMRI) studies of Brooks et al studying thermal pain threshold have shown that when subjects were distracted from thermal pain stimulation, brain activity was lessened (50).

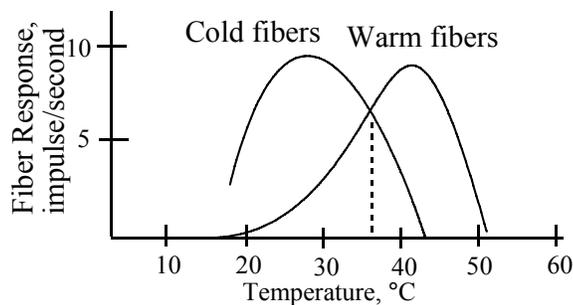


Figure 1.5. Response of warm and cold fibers to temperature stimulus.

Different parts of the body vary in tactile acuity (more sensitive than others) and the acuity is usually measured by the two point threshold. The *two point threshold* is a sensory difference threshold test which measures the smallest separation between two points that can be perceived as two points and can be performed using various instruments that deliver two-point stimuli to the skin at variable distances (51). The mechanoreceptor concentration in various areas of the skin is different

(Figure 1.6) (52), producing varying sensitivity (47). Areas with small receptive fields, such as the lips and fingertips, have greater tactile acuity as the stimulus may affect multiple neurons at once allowing for better perception (Table 1.5) (53). SA I and RA I fibers have small receptive fields found in great abundance in the fingertips accounting for the high acuity in the fingertips (14).

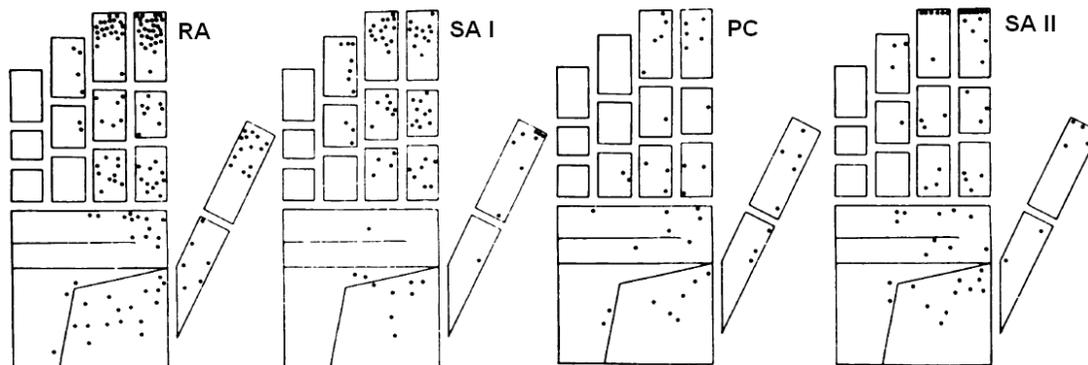


Figure 1.6. Locations of the receptive field centers for various skin mechanoreceptors.

Table 1.5. Two point threshold values for various areas on the body.

Area of Body	Threshold Distance (minimal distance), mm
Tip of tongue	1
Tip of finger	2
Back of hand	38
Along spine	60

Active touch occurs when an individual is actively observing an object by touch, rather than passive where the individual is being touched by the object (Figure 1.7) (53-55). These two forms of touch result in differing perceptions of the object (14). Active touch stimulates skin receptors and other receptors such as those in joints because of the movement of the hand. Active touch is considered purposive, where the individual feels an object with the point of determining its traits, but is equally as effective as passive touch in which the object is moved across the receptors. The terms “touch” or “feel” are usually associated with the concept of active touch, rather than passive (53).

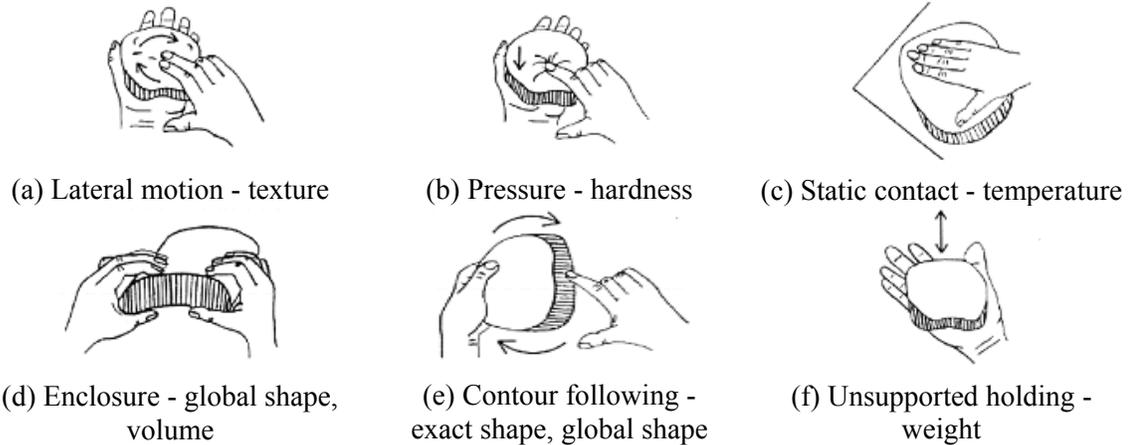


Figure 1.7. Some exploratory procedures.

The ability to identify objects (3D) by touch is referred to as haptic perception. Many people can identify common objects within one to two seconds using touch. Exploratory procedures (EP) are distinctive movements used to identify objects and the type of procedure used depends on the object qualities (Figure 1.7). The exploratory procedures of lateral motion (a) and ‘contour following (e) are usually used to judge texture. Enclosure (d) and contour following (e) procedures are used to judge exact shape (14,56). Other types of procedures may exist such as shaking a box to explore what may be inside or a child rocking a tooth to feel how loose it may be (53). It is, however, easier to identify familiar objects than unfamiliar ones.

Research on sensory perception is now often performed using more than one sense at a time as this simulates real-world situations. The interaction between vision and touch on human perception has been reported. Kennett et al have shown that during two-point tactile discrimination experiment on the arm, the ability to see the arm during the experiment improved performance and increasing the magnification of the arm also improved the resolution of the two points even though the arm could not be seen during the actual application of the stimuli (57). Taylor-Clarke et al have reported visual-tactile experiments that conclude that viewing parts of the body alters the neural activity of somatosensory region of the brain which outlast the visualization (58). Norman et al have

presented experimentation that demonstrated that there was a greater perceptual sensitivity to 3D objects when an object was viewed visually first then observed by touch. They hypothesize that increased sensorial experience produces increased perceptual differentiation and they eliminated the role of cognition by using unfamiliar objects (59).

There are several disorders that affect the sense of touch, which may be related to the sensitivity of the nerves, disorders of the somatosensory cortex, and symptoms of other disorders or illnesses such as tumors in the brain. Many disorders affecting touch are due to accidents or injuries and are very uncommon. Hypoesthesia (numbness) is the partial or total lack of sensation or cutaneous stimulation in a part of the body, and may be attributed to various reasons such as damaged nerves. Paresthesia is a sensation of tingling or pricking of the skin and is usually associated with other illnesses (60).

The sense of smell

Smell (olfaction) is considered a "chemical" sense just as the sense of taste and utilizes hundreds of olfactory receptors, each thought of for binding to a particular molecular feature. This sense is considered a molecule detector and 'gate keeper' as it directly detects gas molecules and is used to determine good or bad molecules that should be allowed into the body. This gate keeper function is associated with emotions and memories (61). The olfactory receptors have a lifespan of 1-3 months, then they are regenerated (24). The olfactory receptor proteins cause reactions that lead to the opening of ion channels, which send signals eventually to the olfactory cortex. Genetic research has concluded that there are 1,000 types of receptor proteins each responding to a small group of odorants and 10,000,000 receptor neurons containing 1,000 similar receptor proteins (14). The purpose of smell for many animals is survival, to a lesser extent in humans. The sense of smell serves also as a warning signal for avoidance of fire and spoilage or alerts to pleasant aromas for approach. Volatility (related to the vapor pressure) is a requirement for any molecule to be observed

by olfaction. The odor threshold of any compound affects at what concentrations we observe it. However, smell and flavor (combination of smell and taste) have more importance to human in a non-crucial manner such as in foods and fragrances.

There are different theories concerning the discrimination of odor intensity and quality, however, that the odor of a substance is generally determined by its structure is widely accepted. Researchers have found that the physical and chemical properties of odorants affect the quality of the odor, however, the specific details of the mechanism has not been determined. Since this relationship has not been determined, focus has been on the correlation between odorant and neural coding. This type of research utilizes odotopes (compounds with a similar chemical feature) and observes neural activity. It has been shown that olfactory receptor neurons respond to a number of odorants and similar neurons are clustered in particular areas of the nasal passage (14).

Table 1.6. Primary odorants and examples described by Amoore.

Primary odorants described by Amoore	Example of odorants
Ethereal	Ether, dichloroethane
Camphoraceous	Camphor, ethers
Musky	Esters
Floral	Alcohols
Minty	Ketones
Pungent	carboxylic acids
Putrid	disulfides, amines

Amoore has studied pure compounds with published aroma descriptions, and characterized them into 14 groups, which were narrowed down into 7 primary odorants groups (Table 1.6) (62). Amoore studied various specific anosmias (persons with olfactory deficiencies in observing specific primary odor groups), and used this research in the classification of aromas (63). There is debate over the existence of primary odors, similar to the concept of primary colors (24). This research included the use of suitable standards with attention to the threshold concentrations and similar odor intensities to make comparisons. His research proposed the stereochemical theory of olfaction which suggests that the structure of the molecule determines the aroma, particularly the physical fit of the

molecules in certain receptors (Figure 1.8) (64). A similar theory has also been proposed by R.W. Moncrieff, however an analysis of chemical differences and properties in the various classes were included in the study such as the reactions and interactions of the molecules (65). The results of these studies are sometimes referred to as the Moncrieff-Amoore site fitting theory (66).

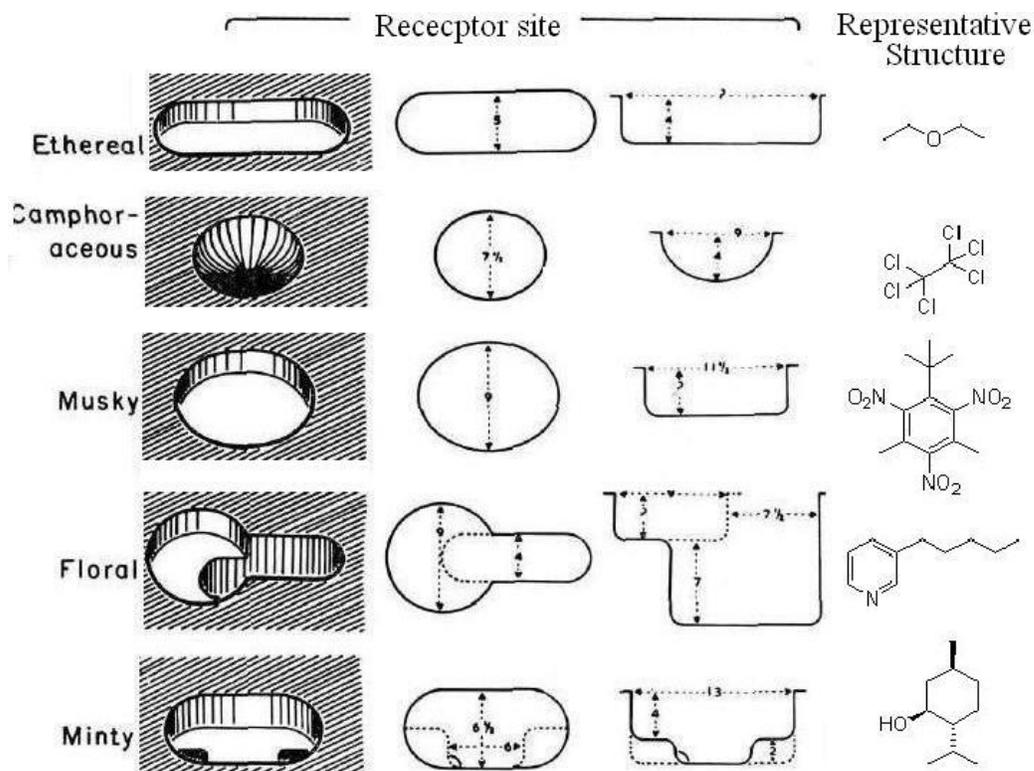


Figure 1.8. Proposed olfactory receptor sites with representative compounds proposed to fit them.

Jennings-White described 38 classes of compounds using the anosmias method, of which 11 were not discussed because they were either discussed sufficiently by Amoore or could not be determined by the anosmia method. This work explored similarities in the molecular structures, and described in more detail a hypothetical explanation for the interactions and structural details of odorants and receptors. For example, acidic odorants must be capable of donating protons at receptor

sites while the presence of electrophilic or nucleophilic regions on molecules is grouped in certain classes of odorants (Table 1.7). This research suggests that odor molecules possess a variety of features and thus excite specific receptors more or less strongly. This combination of excitatory signals from different receptors makes up what we perceive as the molecule's smell (67).

Table 1.7. Some primary odorants and examples described by Jennings-White.

Odorants class	Representative odorants	Characteristic of class
Acidic	Formic acid	Electrophilic, proton donating
Alliaceous	Allyl isothiocyanate	Large hydrophobic region, containing sulfur
Aniseed	Anethole	Non-polar p-disubstituted benzene
Burnt	Pyridine	Nitrogen heteroaromatic ring with lone pair on nitrogen in the plane of the ring
Citrus	3,7-dimethyl-2,6-octadienal (Citral)	Cyclic hydrocarbons or linear with polar function group
Edible	3-hydroxy-2-methyl-4H-pyran-4-one	1,4 disposition of heteroatoms
Fruity	γ -undecalactone	Carbonyl and hydrophobic region
Lily	Hydroxycitronellal	Bifunctional, tertiary alcohol
Oxidizing	Ozone	Electrophilic character
Sweet	Vanillin	Aromatic ring with carbonyl or similar functional group

Other theories on olfaction include the vibrational and radiation theories, however recent research has shown these theories are not valid (68). Vibration theory of olfaction proposes that a molecule's characteristic odor is due to its vibrational frequency in the infrared range as proposed by R.H. Wright (69). The radiation theory proposes that olfaction is a result of the heat released from the organism's receptors and is due to the size and shape of the receptor which results in differing heats released. Substances in the absorption band of this region will lose energy which allows for the stimulation (70).

The *odor threshold values* are the lowest concentration of a compound perceivable 50% of the time to repeated presentations of an odorant by the population. *Odor detection threshold* is the concentration at which 50% of the population can identify the presence of an odor or odorant without

characterizing the stimulus. These two threshold values are often used interchangeably. The *odor recognition threshold* is the concentration at which an odor can be identified or described and is divided into two categories: 50% and 100% odor recognition threshold. A *50% odor recognition threshold* is the concentration at which 50% of the people recognize the odor and the *100% odor recognition threshold* is the lowest concentration at which 100% of trained observers can positively identify an odor (71). These odor threshold values can be expressed as volume of odorant per volume of solvent or air and are usually presented in units of ppm. The odor threshold for the perception of an odor varies with the odor type, but is typically from 2×10^{-7} to 1 ppm of air (66). Table 1.8 includes some characteristic values.

Various methodologies have been used to determine these values. *Direct odor sampling* is performed by sample is fed into an olfactometer (apparatus for measuring by odor concentrations and intensity by smell) for assessment by an odor panel, while indirect sampling uses odor sampling bags. A variety of factors influence the values and ranges significantly obtained from these methods: a) different delivery systems, b) screening of panelist for specific anosmia (inability to smell), c) experience and sensitivity of panelists, d) age and gender of panelists, e) purity of the sample and solvents and f) media used to evaluate the odors (72-74). Vapor pressure, pressure of a vapor in equilibrium with its non-vapor phases at a specific temperature, can give an estimate of the magnitude of the odor threshold values, however, other factors affect these detection limits (74). Certain aromas of compounds such as ammonia and chlorine present a chemical sensation (burning, cooling etc) that is perceived easily even at low concentrations and may sometimes be mistaken as the odor sensation (66). The odor threshold values can be determined by either direct or indirect odor sampling.

Table 1.8. Comparison of the odor thresholds for some common chemicals.

Chemical	Vapor Pressure, mmHg at 20°C	Odor Threshold, ppm	
		Detection range	50% recognition
Amyl alcohol	2	0.10-0.30	1.0
Ammonia	115 (10% solution)	0.037-5.75	46.8
butyl acetate	8	0.006-0.007	0.037
cyclohexanone	2	0.019-0.12	0.12
ethyl acetate	76	0.61-6.3	13.2
methanol	97	4.26-33	53.3
methyl ethyl ketone	2.1	0.27-2.0	5.5

There are several interesting aspects of olfaction that are often overlooked. The human sense of smell is not as sensitive as in many other animals, however, is sensitive enough to detect one molecule per receptor and the lowered sensitivity in human is therefore attributed to a lower number of receptors (14). Humans have the ability to detect differences in odor intensity due to differences in threshold (75). Identification of odorants improves with practice, in that subjects will associate the name with an odor much better after first being corrected after a misidentification (important in designing experiments that involve aromas). Having knowledge of the identification of an aroma tends to transform the perception of the odor (14,75). Unfamiliar odors usually lead to avoidance, but this perception can be changed based on information given to the observer. For example, presentation of pleasant or unpleasant pictures before observation of an aroma alters the perception of the aroma (76). Studies have also shown that ~75% of humans can identify other people by their odor, but not as a sole means of identification (14).

Doty et al have presented data demonstrating that women outperform their male counterparts in odor detection, discrimination and identification tests. This research showed gender differences in the description of pleasant aromas, where women typically described aromas associated with human body fluids such as sweat as unpleasant and intense (75,77,78). Women can also identify aromas with differing abilities during the menstrual cycle, possibly due to hormonal changes or changes in the olfactory epithelium (79). Many enantiomeric pairs of odorants have identical smells; however,

there are many examples of enantiomers that smell completely different as shown in Table 1.9 (80,81). A well known pair of enantiomers showing this property is the *R* and *S* carvones and this pair is often used in olfactory studies as a method of threshold evaluation using persons with and without the ability to smell one or both carvones (82). The biggest problem associated with olfaction research is that characteristics and detectability of aromas are subjective or individual-dependent (24,83), however Walker et al suggest that a larger part of the variation is due to lack of correlation of methods used between laboratories rather than to individuals tested (84).

Table 1.9. Examples of enantiomers showing differing aromas.

Compound	Odor description
7-Hydroxy-6,7-dihydro-citronellal (+)	Lily of the valley with green minty notes
7-Hydroxy-6,7-dihydro-citronellal (-)	Sweet lily of the valley note
Linalool (+)	Sweet, petigrain
Linalool (-)	Woody, lavender
Carvone (+)	Caraway
Carvone (-)	Spearmint
Androstenone (+)	Odorless
Androstenone (-)	Sweaty, urine, strong, musky
Limonene (+)	Orange
Limonene (-)	Turpentine

Olfaction is closely associated with emotional memory and is useful for deciding on avoidance or continuation to observe a substance (61). Savic et al studied cerebral activation during tasks of smelling of odorless air, odors, discrimination of odor intensity and quality using positron emission tomography (PET) and fMRI experiments (brain activation experiments). The results showed that smelling odors activated olfactory regions of the brain, while other olfactory functions such as discrimination of odor and intensity had activated other regions of the brain such as the limbic system (85). PET and fMRI studies of Zald and Pardo have shown that there is an activation of the left part of the amygdala for highly aversive odors and deactivation for neutral or mildly aversive odors, suggesting that the amygdala responds preferentially to highly aversive odors (86). Buchanan et al have presented psychophysical research that demonstrates that the human amygdala

is essential for olfactory memory, where patients with unilateral amygdala damaged were impaired in their memory for matching odors with names, but were not significantly impaired in odor recognition. Persons with bilateral amygdala damage have severe impairment in both odor-name matching as well as in odor recognition memory (87).

Anosmia, which may be due to injury, allergies or infection, is often a difficult disorder to diagnose and treat. The severity of this disorder ranges from the inability to smell one form of chemicals to being unable to smell anything at all and it affects 1-2% of the US population (88). Hyposmia is the decreased ability to observe aromas and may be a result of allergies or colds affecting (temporary) ~5% of the US (89). Hyperosmia is increased sensitivity to aromas which may be caused by illnesses such as migraines. Migraine sufferers (25% of women and 8% of men) often experience hypersensitivity to aromas and these headaches are often triggered by intense aroma (90). Research has shown that migraine sufferers who experience hypersensitivity to odors during migraines also experience hyperacuity between attacks in that they are able to observe aromas at lower concentrations than non sufferers (91).

1.4 Sensory learning

Vision, touch, smell, taste, and audition are automatically integrated into the perception of an event, so human perception is multi-sensory. Some researchers exploring multimodal sensations have noted that revealing where sensory signals are combined and integrated in the brain is key to understanding the basis by which cross-modal processing influences behavior and learning (92). The use of multi-sensory learning takes advantage of all the senses to reinforce learning as each sense builds toward a more complete experience of a concept (93) or an alternative way of experiencing a concept or ideas. Perception of events normally depends on the combination of information from the different sensory systems; however, research has shown that the different sensorial modalities do not

contribute equally to the integrated perception (94). The multi-sensory enhancement possibly encourages learning due to increased attention (95) and the use of more than one sense may encourage learning, if not just to stimulate interest in the concept. Studies conducted by Cann and Ross have shown that olfactory stimuli enhance memory recognition (96). Chu and Downes performed experiments linking better memory retention of aromas to the Proust phenomenon (97). Proust phenomenon is the ability of odors to be spontaneously prompted from autobiographical memories, which were personal accounts of events or memories related to a person's past. This phenomenon is believed to occur due to the fact that memory of odors does not deteriorate as quickly as memories from other senses (98).

Lehmann and Murray performed experiments that suggest that past multi-sensory experiences can enrich current uni-sensory processing and memory performance (99). Their research determined the kinds of multi-sensory experiences necessary to produce distinct memory that can be retrieved upon repetition of the visual component. A review by Shams and Seitz suggests that multi-sensory-training protocols can better approximate natural settings and are more effective for learning. Memory research presented shows that multi-sensory exposure can result in superior recognition of objects when compared to uni-sensory exposure because multi-sensory training can engage individuals with different learning styles (100).

Multi-sensory learning is one way to capitalize on different perceptual learning styles. Research has shown that people have different perceptual learning preferences (visual, auditory and kinesthetic) (101). Auditory learning involves sounds and words, which is traditionally given in a lecture or narrated distance learning course. Some students prefer strategies that involve reading and/or writing. Kinesthetic learning involves using taste, touch, smell, field trips and general laboratory experiences to explore concepts. Research has also shown that most people learn in one or more of these realms and may miss information presented in the others but these learning strategies

can change to other types of learning styles over time (101). However, this multi-sensory approach may potentially benefit students by bringing attention to a learning preference as this research suggests, but more importantly beneficial through increased contact with the material through the use of different modes or sensory exposure.

Dede et al. have used virtual immersion experiments to demonstrate that multi-sensory representations of scientific phenomena is a valuable tool for enhancing understanding of chemistry and physics as well as displacing misconceptions through experiential metaphors and analogies (102). Multi-tool teaching approaches such as multimedia and virtual environments incorporated into traditional lectures have been shown to facilitate diverse educational environments and addressing variety of learning preferences which generates enthusiasm in majority of students (103). Research conducted on chemical engineering courses taught using an instructional model to address the different learning styles suggest that this approach enhanced understanding and promoted the development of thinking skills. It was suggested that with suitable modifications for the differences in course material, the model may be equally effective for chemistry instruction (104).

With the low incidence of sensory disabilities in the population, the inclusion of multiple sensorial experiences in the undergraduate laboratory could increase the chances for students to learn the chemical concepts explored. From the review of the sensory thresholds, it can be seen that sensitivity to small changes such as those that can be observed in chemical reactions can allow students to observe smell, temperature and sound changes. Sensitivity to sensory changes and the ability to discriminate between small changes (due to thresholds) can be used to strengthen the learning experience by manipulating chemistry experiments to allow students to make sensory determinations. Conversely, using these multi-sensory experiments could allow students with various sensory disabilities an opportunity to experience chemistry experiments in richer ways as they can actively make their own observations.

1.5 Proposal

Multi-sensory learning can benefit *all* students by actively engaging them in learning through stimulation or through their different learning styles (101-104). Multi-sensory exposure in the laboratory can engage individuals with different learning styles and potentially increase memory retention (100). Manipulation of typical chemical experiments to use multiple senses can be mentally stimulating for students potentially allowing for better memory retention similar to results found by multi-sensory input in virtual environment experiments (105). Since perception generally depends on information from the different sensory systems, multi-sensory experiences in the laboratory exploits all the senses for investigating chemical concepts, making qualitative determinations and familiarizing students with chemical techniques. These experiments could potentially reinforce learning since each sense builds toward a more complete experience of concepts (93).

A variety of experiments were researched and concepts explored using traditional experiments as a foundation as well as investigating exciting literature relevant to the development of sensorial experiments. Several sensorial experiments were developed to utilize multiple or different senses in making chemical determinations. Each experiment was designed to use one or more sense other than eyesight, and modifications were made for portions of the experiment that require eyesight such as the use of a talking thermometer or light probe. The research objectives of this dissertation project were both chemical and pedagogical in nature. The chemical objectives, which included evaluation of hazards, accuracy of the data, and examination of the chemistry of the experiments, were developed to ensure students have a similar laboratory experience to traditional experiments. These experiments were implemented into the undergraduate laboratories and pilot testing showed necessary modifications. Interventions and modifications were made in response to observations made during implementation.

These experiments were designed to also give students a high-quality learning experience by developing and stimulating students' conceptual understanding and promoting students' critical thinking skills. An educational framework was used to develop an useful laboratory format. The format allowed instructors to observe students' conceptual changes through their responses to conceptual questions. These conceptual questions were developed to explore students' understanding of macroscopic, particulate, and symbolic representations. The experiments provided an inquiry-experience where students work collaboratively and students' common were addressed misconceptions in conceptual questions and interventions. Implementation and assessment of this new laboratory format were conducted in order to evaluate its effectiveness.

REFERENCES

1. Wood, J. T.; Eddy, R. *J. Chem. Edu.* **1996**, *73*, 257–258.
2. Neppel, K.; Oliver-Hoyo, M. T.; Queen, C.; Reed, N. *J. Chem. Edu.* **2005**, *82*, 607.
3. Flair, M.; Setzer, W. N. *J. Chem. Edu.* **1990**, *67*, 795–796.
4. Rancke-Madsen, E., Krogh, J.A. *Acta Chem. Scand.*, **1956**, *10*, 495-499.
5. Anderson, M.; Buckley, A. *J. Chem. Edu.* **1996**, *73*, 639-640.
6. Hiemenz, P. C.; Pfeiffer, E. *J. Chem. Edu.* **1972**, *49*, 263.
7. Tallman, D. E. *J. Chem. Edu.* **1978**, *55*, 605.
8. Ratliff, J. L. *J. Chem. Edu.* **1997**, *74*, 710.
9. Anderson, J. L. *J. Chem. Edu.* **1982**, *59*, 871.
10. Davies, R. A., John, N. W., MacDonald, J. N., Hughes, K. H., **2005**, Proceedings of the tenth international conference on 3D Web technology: 3D technologies for the World Wide Web, 143–150.
11. Sato, M.; Liu, X.; Murayama, J.; Akahane, K.; Isshiki, M. *LNCS Transactions on Edutainment I*, **2008**, *5080*, 28–39.
12. Jones, G. M.; Andre, T.; Superfine, R.; Taylor, R. *J. Res. Sci. Teach.*, **2003**, *40*, 303.
13. <http://www.molysym.com/> Last accessed on October 30th 2007;
<http://www.nsti.org/Nanotech2004/showabstract.html?absno=873> Last Accessed on October 30th 2007.
14. Goldstein, E.B. *Sensation & Perception*, 5th ed. Brooks/Cole Publishing Company, California, 1999.
15. David J. Echevarria, *Sensation and Perception*, Chapter 1, Spring 2008;
<http://www.usm.edu/neurolab/CourseMaterials.html>; (accessed August 2008).
16. Moskowitz, H. R. *Crit. Rev. Food Sci. Nut.*, **1977**, *9*, 41-79.
17. Ehrenstein, W. H., Ehrenstein, A. *Psychophysical Methods*, Chapter 43, <http://www.optics-vision.gr/pdf/PSYCHOPHYSICAL%20METHODS.pdf>; Information Processing in Human Perceptual Motor Performance, Lecture 2, <http://www.ahs.uwaterloo.ca/~kin356/Lecture2.pdf>, (accessed June 2008).

18. Sensory Thresholds. <http://www.cliffsnotes.com/WileyCDA/CliffsReviewTopic/topicArticleId-25438,articleId-25322.html>. (accessed September 2008).
19. Fechner, G. *Psychological Research*, **1987**, 49, 213-219.
20. Teghtsoonian, R. *Psych. Rev.*, **1971**, 78, 71-80.
21. Weber's Law of Just Noticeable Differences, <http://www.usd.edu/psyc301/WebersLaw.htm>, (accessed September 2008).
22. Examples of research on cerebral cortex as it related to perception. Parker, A. J. *Nature Reviews Neuroscience*, **2007**, 8, 379-391.; Engineer, C. T.; Perez, C. A.; Chen, Y. H.; Carraway, R. S.; Reed, A. C.; Shetake, J. A.; Jakkamsetti, V.; Chang, K. Q.; Kilgard, M. P. *Nature Neuroscience*, **2008**, 11, 603-608.; Butler, S. R. *Brit. Med. J.* **1971**, 4, 544-7.; Parker, A., J., Krug, K. *Current Opinion in Neurobiology*, **2003**, 13, 433-439. Caselli, R. *Mayo Clinic proceedings*. **1991**, 66, 129-42.
23. Martini, F. H. *Fundamentals of Anatomy & Physiology*, 5th Edition, **2001**, Chapters 16-17, Prentice Hall, NJ.
24. Soderquist, D.R. *Sensory Processes*, **2002**. Sage Publications, California.
25. The Eye, <http://www.csulb.edu/~cwallis/482/visualsystem/eye.html>; (accessed June 2008).
26. Weale, R. A. *Ann. R. Coll. Surg. Engl.* **1961**, 28, 16-35.
27. Kolb, H., Fernandez, E., Nelson, R. Webvision: Light and Dark Adaptation, updated February 2008, http://webvision.med.utah.edu/light_dark.html; (accessed September 2008).
28. Rushton, W. A. H. *J. Physiol.*, **1972**, 220, 1-31.
29. Barlow, H. B. *Nature*, **1957**, 179, 255 – 256; Anstis, S. *Vision Research*, **2002**, 42, 2485-2491.
30. human eye. Encyclopedia Britannica. 2008. <http://www.britannica.com/EBchecked/topic/199272/eye>; (Accessed June 2008).
31. Young-Helmholtz three-colour theory Encyclopedia Britannica, 2008, <http://www.britannica.com/EBchecked/topic/654047/Young-Helmholtz-three-colour-theory>; (accessed June, 2008).
32. Wald, G. Brown, P. *Science*, **1958**, 127, 222-249; Wald, G. *Nature*, **1968**, 219, 800 – 807.
33. Ewald Hering, Encyclopædia Britannica Online, 2008, <http://www.britannica.com/EBchecked/topic/263047/Ewald-Hering>. (accessed September 2008).

34. Color vision deficiency, Reviewed March 2006,
<http://ghr.nlm.nih.gov/condition=colorvisiondeficiency>; Vision Problems, Updated September, 2006, <http://www.nlm.nih.gov/medlineplus/ency/article/003029.htm>; (accessed June 2008).
35. Eye Conditions, <http://www.ceilasik.com/celc-conditions.htm>, (accessed June 2009); Agnosia, http://www.psychnet-uk.com/dsm_iv/agnosia.htm, (accessed September 2008); Ghadiali, R. *ACNR*, **2004**, 4, 18-20.
36. *Wrong Diagnosis: Statistics on Myopia; Statistics on Astigmatism; Statistics on Hyperopia*, updated January 21st 2009, http://www.wrongdiagnosis.com/m/myopia/stats.htm#medical_stats; http://www.wrongdiagnosis.com/h/hyperopia/stats.htm#medical_stats; <http://www.wrongdiagnosis.com/a/astigmatism/stats.htm>; (accessed January, 2009).
37. *Unite For Sight Refractive Error Module*,
<http://www.uniteforsight.org/course/refractiveerror.php>; (accessed June, 2008).
38. human ear, Encyclopedia Britannica, 2008,
<http://www.britannica.com/EBchecked/topic/175622/ear>; (accessed June 2008).
39. sound. Encyclopædia Britannica Online. 2008,
<http://www.britannica.com/EBchecked/topic/555255/sound>. (accessed September 2008).
40. Geldard, F. *The Human senses*, 2nd edition, 1972, John Wiley & Sons, Inc., New York.
41. Noise exposure associated with marching and pep bands: measurements, assessment of risks, and possible solutions; <http://www.duke.edu/~jak21/physics.html>, (accessed September 2008).
42. MedlinePlus: Hearing, Ear Infections, and Deafness, NIDCD, updated 2008,
<http://www.nidcd.nih.gov/health/hearing/>; (accessed June, 2008).
43. *An Educator's Guide to Hearing Disability Issues*,
<http://www.ed.uiuc.edu/wp/access/hearing.html>; (accessed June, 2008).
44. *Hearing Loss May Be More Widespread Than Thought*, updated 2000,
http://www.nlm.nih.gov/medlineplus/news/fullstory_67460.html; (accessed September, 2008).
45. *Hearing Loss*, updated July 2008; <http://www.dizziness-and-balance.com/disorders/hearing/hearing.html>; (accessed January 2009).
46. Reed, C. M.; Rabinowitz, W. M.; Durlach, N. I.; Braida, L. D.; Conway-Fithian, S.; Schultz, M. C. *J. Acoustical Soc. Am.* **1985**, 77, 247-57.
47. *The Two-Point Threshold: Touch Acuity*, updated November 29th, 2007,
<http://www.usd.edu/coglab/2point.html>, (accessed September 10th, 2008).
48. Tominaga, M.; Caterina, M. J. *J. Neurobiology*, **2004**, 61, 3-12.

49. Sarlani, E.; Farooq, N.; Greenspan, J. D. *Pain*, **2003**, *106*, 9-18.
50. Brooks, J. C. W.; Nurmikko, T. J.; Bimson, W. E.; Singh, K. D.; Roberts, N. *NeuroImage*, **2002**, *15*, 293-301.
51. Tannan, V.; Dennis, R.; Tommerdahl, M. *J. Neuroscience Methods*, **2005**, *147*, 75-81.
52. Johansson, R.S., Vallbo, A. B. *J. Physiol.* **1979**, *28*, 283-300.
53. Dashiell, J. F., *Fundamentals of objective psychology*, 1928, Houghton Mifflin Company, Boston, 79-118.
54. Carneiro, M. M., Velho, L. *Infor. Tech. Disab. E-Journal*, 2004, <http://www.rit.edu/~easi/itd/itdv10n2/carneiro.htm>;
55. Klatzky, R., Bajcsy, R., Lederman, S. *IEEE Inter. Confer. Robotics & Automation*. **1987**, 1806-1809.
56. Kilgour, A. R., Lederman, S. J. *Perception & Psychophysics*, **2002**, *64*, 339-352
57. Kennett, S., Taylor-Clarke, M., Haggard, P., *Curr. Biol.*, **2001**, *11*, 1188–1191.
58. Taylor-Clarke, M.; Kennett, S.; Haggard, P. *Neuroscience Letters*, **2004**, *354*, 22-25.
59. Norman, J. F., Clayton, A. M., Normal, H. F., Crabtree, C. E. *Perception*, **2008**, *37*, 185-196.
60. Symptom: Paresthesias, updated 2007, <http://www.cureresearch.com/sym/paresthesias.htm>; (accessed June, 2008).
61. Cann, A., Ross, D. *Amer. J. Psychol.*, **1989**, *102*, 91-102.; Chu S., Downes J. *Mem. Cognit.*, **2002**, *30*, 4, 511–518.
62. Amoore, J.E., Venstrom, D. *J. Food Sci.* **1966**, *31*, 118-28.
63. Amoore, J. E. *Chem. Sens. Flavor*, **1977**, *2*, 267-281.
64. Amoore, J. E. *Nature*, **1963**, *198*, 271 – 272.
65. Moncrieff, R. W. *J Physiol.* **1954**, *28*; *125*, 453–465.
66. Roderick, W. R. *J. Chem. Educ.* **1996**, *43*, 510-520.
67. Jennings-White, C. *Perfumer & Flavorist*, **1984**, *9*, 46-58.
68. Briggs, M. H., Duncan, R. B. *Nature*, **1961**, *191*, 1310., Buijs, K., Schutte, C. J. H., Verster, F. *Nature*, **1961**, *192*, 751.

69. Wright, R.H. *Nature*, **1961**, 190, 1101 – 1102.
70. Beck, L. H., Miles, W. R. *Science*, **1947**, 106, 511.
71. Heinsohn, R.J., Cimbala J. M. *Indoor Air Quality Engineering: Environmental Health and Control of Indoor Pollutants*, CRC Press, 2003, 232-235.; Iowa State: Animal Agriculture and Air Quality, 2006, <http://www.extension.iastate.edu/airquality/pubs.html>, (accessed December 2007).
72. Takeoka, G.; Buttery, R.G.; Ling, L. *Food Sci. and Tech.* **1996**, 52, 677-680; Takeoka, G.; Buttery, R.G.; Turnbaugh, J.G.; Benson, M. *Food Sci. and Tech.* **1995**, 28, 153-156; Salo, P.; Nykänen, L.; Suomalainen, H. J. *Food Sci.* **1972**, 37, 394-398;
73. Measurement of Odor Threshold by Triangle Odor Bag Method.
http://www.env.go.jp/en/air/odor/measure/02_3_2.pdf, (accessed December 2007).
74. Tsukatani, T., Miwa, T., Furukawa, M., Costanzo, R. M. *Chem. Senses*, **2003**, 28, 25–32.
75. Richard L. Doty, Psychophysical measurement of odor perception, In *The Human Sense of Smell*, D.G. Laing, R.L. Doty and W. Breipohl., Eds; Berlin, Springer-Verlag, **1991**; pp 91-134.
76. Pollatos, O., Kopietz, R., Linn, J., Albrecht, J., Sakar, V., Anzinger, A., Schandry, R., Wiesmann, M., *Chem. Senses*, **2007**, 32, 583–589.
77. Doty, R. L.; Steven Applebaum; Hiroyuki Zusho; R. Gregg Settle; *Neuropsychologia*. **1985**, 23, pp 667-672.; Doty, R. L.; Kara-Lynne Kerr; *Neuropsychologia*, **2005**, 43, pp 1749-1753.
78. Doty, R. L.; *Chem. Senses*, **1997**, 22, 565-586.
79. Pause, B.M., Sojka, B., Krauel, K., Fehm-Wolfsdorf, G., Ferstl, R. *Biological psychology*, **1996**, 44, 31-54., Navarrete-Palacios, E.; Hudson, R.; Reyes-Guerrero, G.; Guevara-Guzman, R. *Biological psychology*, **2003**, 63, 269-79.
80. Brenna, E., Fuganti, C., Serra, S. *Tetrahedron: Asymmetry*, **2003**, 14, 1–42.
81. Sell, C. S. *Chemistry & Biodiversity*, **2004**, 1, 1899-1920.
82. Pelosi, P., Viti, R., *Chemical Senses and Flavor*, **1978**, 3, 331-337.
83. Stevens, J. C., Cain, W. S., Burke, R. J. *Chemical Senses*, **1988**, 13, 643-653.
84. Walker, J. C., Hall, S. B., Walker, D. B., Kendal-Reed, M. S., Hood, A. F., Niu, X. *Chem. Senses*, **2003**, 28, 817–826
85. Savic, I. *Current Opinion in Neurobiology*, **2002**, 12:455–461.; Savic, I., Gulyas, B., Larsson, M. Poland, P. *Neuron*, **2000**, 26, 735–745.

86. Zald, D. H., Pardo, J. V. *Proc. Natl. Acad. Sci. USA*, **1997**, *94*, 4119-4124.; Zald, D. H., Pardo, J. V. *Int J Psychophysiol*, **2000**, *36*, 165-181.
87. Buchanan, T. W. Tranel, D., Adolphs, R. *Learn. Mem.* **2003** *10*: 319-325
88. Smell Dysfunction Glossary of Terms;
<http://www.senseofsmell.org/feature/whitepaper/disorders.php>; (accessed January 2009)
89. Statistics on Taste and Smell, <http://www.nidcd.nih.gov/health/statistics/smell.asp>; (accessed January 2009).
90. Who and How many? Migraine Statistics; <http://www.relieve-migraine-headache.com/migraine-statistics.html>; (accessed January 2009).
91. Snyder, R. D., Drummond, P. D. *Cephalalgia*; **1997**, *17*, 729-732.
92. Bizley, J. K., Nodal, F. R., Bajo, V. M., Nelken, I., King, A. *J. Cerebral Cortex*, **2007**, *17*, 2172—2189.
93. Santangelo, V., Spence, C. *J. Exp. Psychology: Human Percep. Perform.*, **2007**, *33*, 1311–1321.; Moats, L. C., Farrell, M. L., Multisensory Instruction In *Multisensory teaching of basic language skills*, Birsh, J. R. Paul H. Brookes Publishing Co., MA, 2000. Chapter 1.
94. Bresciani, J., Dammeier, F., Ernst, M. O. *Brain Research Bulletin*, **2008**, *75*, 753–760.
95. Guest, S., Spence, C. *Intern. J. Psychophysiology*, **2003**, *50*, 63–80.
96. Cann, A., Ross, D. *Amer. J. Psychol.*, **1989**, *102*, 91-102.
97. Chu S., Downes J. *Mem. Cognit.*, **2002**, *30*, 4, 511–518.
98. Doop, M., Mohr, C., Folley, B., Brewer, W., Park, S. *Olfaction and Memory*, Chapter 4, Brewer, W., Pantelis, C., Castle, D. (eds) *Olfaction and the Brain*, Cambridge University Press, Cambridge, 2006.
99. Lehmann, S., Murray, M. M. *Cognitive Brain Research*, **2005**, *24*, 326–334.
100. Shams, L., Seitz, a. R. *Trends in Cognitive Science*, **2008**, *12*, 411-417.
101. Felder, R.M. Silverman, L.K. *Engr. Education*, **1988**, *78*, 674-681; Felder, R.M. *J. College Science Teaching*, **1993**, *23*, 286-290.; Lowery Bretz, S. *All Students are Not Created Equal: Learning Styles in the Chemistry Classroom*, Eds. Pienta, N. J., Cooper, M. M., Greenbowe, T. J. Chapter 3, in *Chemists' guide to effective teaching*, Pearson Education Inc., NJ, 2005.
102. Dede, C., Salzman, M. C., Loftin, R. B., Sprague, D. *Multisensory Immersion as a Modeling Environment for Learning Complex Scientific Concepts*, http://www.virtual.gmu.edu/ss_pdf/feurzeig.pdf, (accessed August 2008).

103. Trindale, J.; Fiolhais, C.; Almeida, L. *British Journal of Educational Technology*, **2002**, *33*, 471-88.; D'Arcy, C. J.; Eastburn, D. M.; Bruce, B. C. *College Teaching*, **2009**, *57*, 56-63.; Dunn, R.; Honigsfeld, A.; Doolan, L. S.; Bostrom, L.; Russo, K.; Schiering, M. S.; Suh, B.; Tenedero, H. *J. Educ. Strategies: Issues and Ideas*, **2009**, *82*, 135-140.; Garcia-Ros, R.; Perez, F.; Talaya, I. *Electronic J. Res. Educ. Psych.* **2008**, *6*, 547-570.
104. Felder, R. M. *J. Chem. Edu.* **1996**, *73*, 832-836.
105. Dinh, H., Walker, N., Kobayashi, C. S., Hodges, L. A. **1999**, "Evaluating the importance of multi-sensory input on memory and the sense of presence in virtual environments," *Proceedings of the IEEE Virtual Reality Conf.* 222-225.

CHAPTER 2 . Project overview

2.1 Chemical and pedagogical considerations

The research objectives of this dissertation were both chemical and pedagogical. Several chemical considerations were taken into consideration while developing the sensorial experiments to ensure issues of safety and accuracy in these experiments were addressed just as in traditional experimentation. A discussion of these chemical goals as they applied to each sensorial experiment will be discussed in Chapter 3.

a) *Exploration of chemical principles via sensorial changes.* These experiments are similar to experiments currently performed in undergraduate laboratories; however the chemistry is manipulated in order to allow the students to explore reactions and principles with senses other than eyesight. These experiments were developed with the aim of using one or more senses rather than or in addition to sight. The sense of smell was the most commonly used owing to vast amount of mostly organic compounds with characteristic aromas, but the other senses such as the sense of touch were also employed. For example, the sound of the reaction of Na_2CO_3 with an acid was used to determine the presence of a carboxylic acid, or determining the presence of a compound by its characteristic aroma were typical manipulations used to study overall concepts. The ability to utilize these multi-sensory determinations aimed to benefit learning by mentally stimulating students and potentially allowing better memory retention (93).

b) *Evaluation of hazards.* In order to develop sensorial experiments, several issues involving safety were taken into consideration. The experiments were thoroughly screened by carefully comparing effectiveness and hazards of the chemicals used, as they rely on senses traditionally not employed in the laboratory setting. For students to be able to perceive the smell of various compounds these must be volatile, however of low inhalation toxicity. The chemicals used could not

be obnoxious, since aroma control and aroma fatigue would be of concern. Various methods were employed to reduce exposure to aromas to prevent aroma fatigue and to control excessive aromas released into the laboratory. Students were taught to waft chemicals and various chemicals were placed in dropper bottles or in fume hoods to prevent environmental saturation. The experiments were carried out on a small scale in order to reduce accidents and other hazards (2). Performing the experiments on a small scale also means less exposure to chemicals and fewer chemicals were wasted (3). In order to develop small scale experiments, the experimental procedures generally used were altered or even changed to accommodate for small glassware used.

c) *Consideration of adaptation measures and accessibility.* Materials and equipment used were inexpensive and readily accessible to aid implementation and adaptation. Expense and availability of chemicals in comparison to traditional experiments were considered in order to promote their adoption and incorporation into the undergraduate laboratory curriculum. Chemicals used included household or grocery items and common chemicals found in undergraduate laboratory stock rooms. The equipment used was either currently utilized in traditional laboratory settings such as stir hot plates, typical chemical glassware and thermometers or inexpensively purchased such as talking thermometers and light probes. The experiments were designed to allow for easy adaptation into the laboratory to be run along side or instead of traditional experiments even in large universities that generally have large numbers of experiments running at the same time. To allow for this, the set-up of the experiment was generally similar or as simple as that of traditional experiments.

d) *Accuracy and precision of data.* An important aspect of testing these experiments was to ensure that the results were as accurate as traditional experiments and not give students misleading results. Rigorous testing was done on every sensorial experiment to ensure that the resulting data allow students to draw the same conclusions as traditional experiments. The result of the testing will be shown in Chapter 3.

Educational goals were established for these sensorial experiments to provide the ability to develop and stimulate students' conceptual understanding of the concepts. The concepts explored in the experiments could not be diluted by the multi-sensory dimension, but rather enhanced by deeper understanding and promotion of scientific curiosity. These experiments were also designed to promote students' critical thinking skills. Pedagogical goals of this research project included using investigative methods to explore the nature of chemical reactions and determinations, promoting collaborative group work, and designing inquiry-based rather than verification ('recipe-like') experiments. The application of these educational goals to the sensorial experiment will be discussed in Chapter 3. These goals included:

- a) *Establishment of an educational framework.* Several educational frameworks were explored in order to establish practical education goals and develop reasonable assessments. In choosing a framework it was critical that it would allow for the incorporation of the pedagogical goals involving inquiry, investigative skills and foundation for the lab report. Critical thinking, self-analysis and knowledge construction were deemed essential. The framework chosen needed to be supported by educational research and to provide focus in developing educational objectives. The Marzano and Kendall taxonomy was chosen and this framework will be discussed in Section 2.2.
- b) *Evaluation of terminology and misconceptions.* Misconceptions are ideas or concepts which differ from what is generally scientifically acceptable and persists even after correct instruction is given (4). Students may form these alternative conceptions before or after instruction and for a variety of reasons. These misconceptions interfere with the students learning of chemistry and ultimately may cause misunderstanding about other topics as the information becomes cumulative (4). A thorough examination of the literature for these common misconceptions and potential interventions for these misconceptions were investigated. From this research, a variety of

interventions were developed to remedy or prevent alternative conceptions throughout the experiment.

c) *Adoption of investigative inquiry-based experimental approach, rather than verification experiments.* Students investigated principles using multiple senses and drew conclusions about the chemistry rather than using equipment or machines to perform verification labs. These experiments were designed to encourage students to be active learners in the laboratory. Utilizing investigative experiments rather than using instruments for confirmations, allows students to build critical thinking skills essential for a scientist when evaluating a problem (5). Practical science investigations give the opportunity for students to articulate, question and discuss ideas in order to create active learners (6). Herman presents guidelines for redesigning traditional experiments into investigative labs, where the educational strategy is to build on the knowledge the student already possesses (7). An inquiry-based format was utilized for the sensorial experiments in which the focus of the learning lies on the students been actively involved in the experiment, where as in traditional experiments students follow the instructor's direction (8). Several categories for inquiry-driven experiments were seen in the literature such as guided, design-based and open-ended inquiry. Guided-inquiry experiments may provide detailed experimental procedures, but will pose investigative questions for analyzing experimental results (9). Design-based inquiry involves students making choices on the experimental procedure performed, while open-ended inquiry involves students entirely creating their own procedures and investigate the results.

There are various examples of successfully used inquiry-based experiments in undergraduate laboratories (8). Two guided-inquiry experiments described by Mohrig et al. demonstrate the use of student knowledge to predict the outcome of a reaction and using modern technology to verify them (9). Rosenberg has shown a sodium borohydride reduction of a ketone and phenyl magnesium Grignard addition to carbonyl compounds as guided-inquiry experiments (10). Students identify

unknowns by the products of the reactions based on physical properties and use their data to deduce the reactivity of various carbonyls and propose plausible mechanisms. Bopegedera describes discovering gas laws through experiments instead of the conventional approach of using the lecture to teach these concepts (11). In a green chemistry experiment, students have to design laboratory procedures to use in order to examine a scientific question. Students defend their choices in writing and learn why each part of a lab report is necessary (12). A comparison study by Cacciatore and Sevian has shown that who students performed one inquiry stoichiometry experiment out-perform students in the traditional format on stoichiometry content problems and experimental design tasks (13). They suggested that larger improvements in students' performance could be accomplished by increasing the number and variety of inquiry experiments. Herman's guidelines are also useful for developing an inquiry-format, where students plan the details of their experiment within the general guidelines of the instructor or where the hypothesis or analysis of the experiment is open-ended (7). In our sensorial experiments design, students will decide on their own the path to take in the experiment based on their knowledge of the chemistry (designed-based) or provide their own analysis or hypothesis for experimental results (guided-inquiry).

d) *Promotion of collaborative group work.* Each sensorial experiment was designed for students to work in groups of 2-3 (14) in order to achieve a collaborative learning experience. However, even though students work collaboratively to obtain results, they individually write their own lab reports in their own words. Cooper provides an overview of collaborative learning and proposes advantages such as the development of higher-level thinking, and increased student retention (15). Research has shown that collaborative small-group work can be a successful method for students to learn science and hence increase their understanding (16). In these environments, students may be required to teach their peers which increase their own understanding as well as allowing exchange of ideas and active participation in activities. Some examples of collaborative

learning include a project-based laboratory experiment as described by Giancarlo and Slunt in which students figure out the composition of an unknown metal knob ingested and recovered from a puppy (17). The students decide on how to analyze the metal and use two different analytical methods. A peer-developed and led laboratory for general chemistry students has been shown to give students opportunities to not only perform independent research, but successfully worked in groups (18). The students used the motivation from the groups to excel with increased engagement as well as a chance to see how chemists approach problems by working together in a collaborative fashion.

e) *Development of a laboratory writing format.* With the other educational goals in mind, a lab writing format was developed that allows for students to be active participants in their learning as well as aid in the development of critical thinking skills. The format allows students to take more responsibility for their learning of the concepts by through their own construction of knowledge and reflective thinking on the concepts learned. The format allows students to reflect on their knowledge in order to draw scientifically acceptable conclusions about the concept. The cognitive-centered design of the lab report, based on the taxonomy of Marzano and Kendall, allowed for students to develop conceptual knowledge and learn scientific thinking skills (19). The lab reports gave students a model for writing their reports in order to produce meaningful scientific writing. The report also benefited the instructor, allowing the instructor to monitor the students' thought processes and be able to re-develop the experiment accordingly. The Learning Lab Report format was developed to address these issues and is discussed in Section 2.3.

2.2 Educational framework, objectives and assessments

The framework and objectives of the sensorial experiments developed in our laboratory were fashioned on the taxonomy of educational objectives by Marzano and Kendall (20) and the application of which is demonstrated in Chapter 3. Taxonomies are used by instructors to help them

gain perspective on the emphasis or focus needed in the development of instructional material (21). The taxonomy by Marzano and Kendall (M&K) is based on a two dimensional model of thinking skills applied to three types of knowledge which involve a range of factors that affect thinking and behavior. The educational objectives can be classified within these two dimensions. The taxonomy describes the model of behavior involved in engaging in a specific task and the information processed as a result of this decision of engaging in the task.

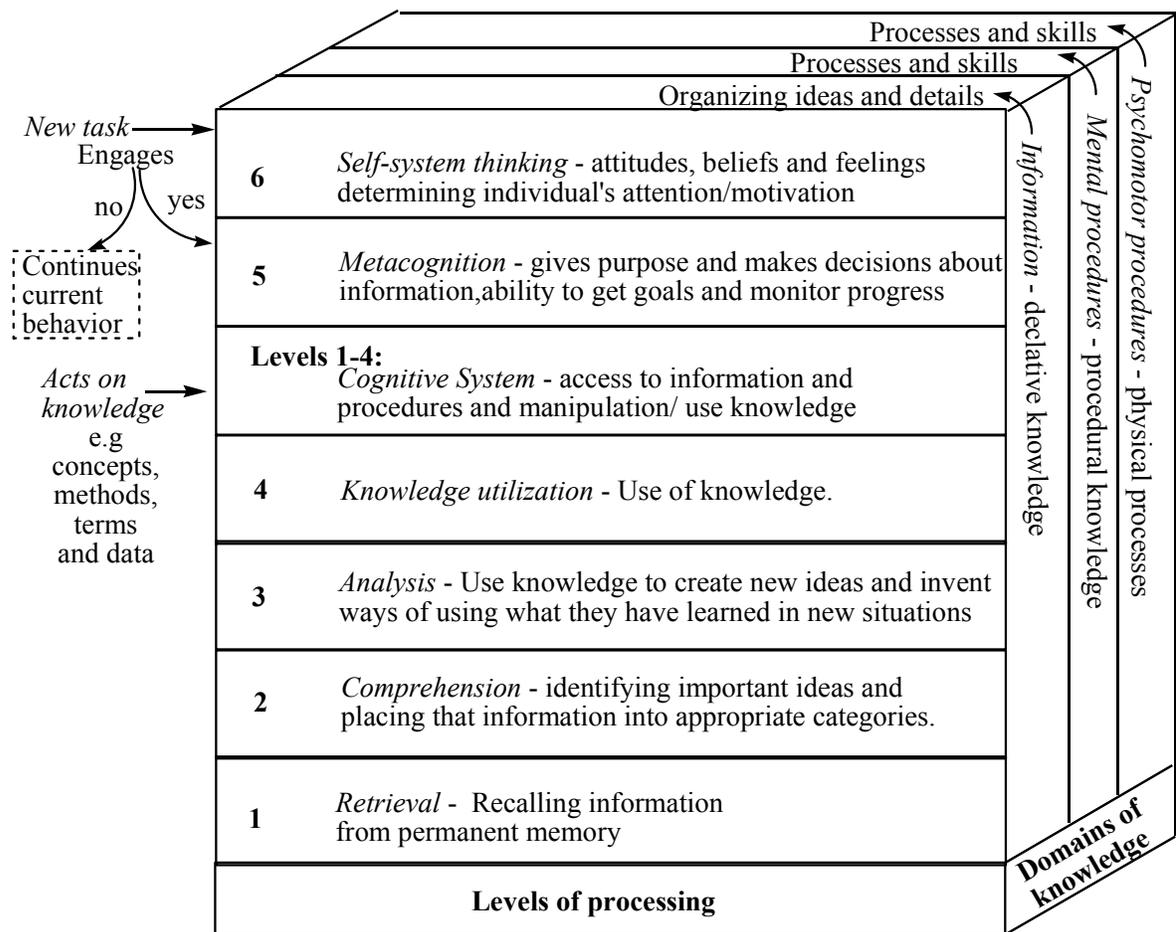


Figure 2.1. The M&K's systems of thought levels and domains of knowledge.

M&K present tools for classifying learning objectives, creating assignments, and teaching critical skills utilizing the concept that knowledge construction consists of three systems of thinking or thinking frameworks: self-system, metacognitive, and cognitive. The taxonomy is composed of 6

hierarchical levels within these systems with four of these levels in the cognitive system (Figure 2.1). Each level is composed of and defined by various mental operations, where level 1 is automatic but levels 2-6 require conscious control. The taxonomy postulates that there are three different types of knowledge or knowledge domains (information, mental procedures, and psychomotor procedures) and the thinking levels have different impacts on each of the knowledge domains (Figure 2.1).

The self-system thinking system involves the attitudes, beliefs and feelings that determine an individual's attention and motivation to complete a task or action (20,22,23). It consists of examining importance, efficacy, emotional responses, and motivation as shown in Table 2.1 (20). When students are confronted with a task, they examine its importance, followed by examining the belief in their capabilities to execute a specific task (referred to as self-efficacy) (24). *Importance, efficacy,* and *emotions* contribute to motivation and the level of motivation is gauged by the degrees of the other self-system mental actions. After a task is deemed as important enough to take part in, metacognition thinking is engaged. Self-system thinking resembles Posner's conceptual change (learning that changes an existing conception) and encompasses Bandura's social-cognitive theory of learning. Posner's theory suggests that for conceptual change to occur students must become dissatisfied with their existing concepts, new concepts must appear intelligible and plausible to the students and the new concept must be fruitful towards the research or investigation (25). The social-cognitive theory involves the interaction of the students' self-system thinking, behavior and environment, where the self-system thoughts affect along with metacognition affect learning (26).

The metacognitive system gives purpose and makes decisions about which information and cognitive processes are necessary. This system allows for the ability to set goals, monitor progress, and evaluate, as it involves executive-like control over cognitive functions. The metacognitive system is divided into four mental operations (Table 2.1) and once engaged, continually interacts with and affects the cognitive system (20,27). The cognitive thinking system gives access to the

information and procedures in memory and helps students manipulate and use knowledge. M&K divide the cognitive system into four mental operations: knowledge retrieval, comprehension, analysis, and knowledge utilization (Table 2.1), where each operation consists of the previous process(es), but do not represent levels of complexity. Hierarchic nature of the cognitive system is defined by the level of consciousness of information processing necessary for control over each preceding cognitive level.

Table 2.1. Description of taxonomy levels of M&K and students' mental operations relative to knowledge domains expressed as educational objectives.

Systems	<i>Mental operations</i>	<i>Students will be able to:</i>
Self-system thinking	Examining importance	Identify and rationalize importance of the knowledge.
	Examining efficacy	Identify and rationalize beliefs about ability to improve competence or understanding relative to knowledge.
	Examining emotional response	Identify and rationalize emotional responses to knowledge.
	Examining motivation	Identify and rationalize overall levels of motivation to improve competence or understanding.
Metacognition	Specifying goals	Establish a goal relative to the knowledge and plan for accomplishing it.
	Monitoring process	Monitor the execution of specific goals.
	Monitoring clarity	Determine the extent of clarity of knowledge.
	Monitoring accuracy	Determine the extent of knowledge accuracy.
Cognition		
Knowledge utilization	Making decisions	Make decisions with or about knowledge.
	Solving problems	Solve problems with or about knowledge.
	Experimenting	Generate and test hypothesis with or about knowledge.
	Investigating	Conduct investigation using knowledge.

Table 2.1. Description of taxonomy levels of M&K (continued).

Systems	Mental operations	Students will be able to:
Analysis	Matching	Identify important similarities and differences.
	Classifying	Organize knowledge into useful categories.
	Analyzing errors	Identify errors in presentation and use of knowledge.
	Generalizing	Construct new generalizations and principles.
	Specifying	Identify specific applications or logical consequences of knowledge.
Comprehension	Integrating	Distill knowledge to critical characteristics in a generalized form.
	Symbolizing	Construct accurate symbolic representation of knowledge, differentiating critical and non-critical components.
Retrieval	Recognizing	Recognize features of information, but not necessarily to understand the knowledge and what is critical.
	Recalling	Produce features of information, but not necessarily to understand the knowledge and what is critical.
	Executing	Perform a procedure without significant error, but not necessarily to understand the logistics.

Knowledge plays a role in the ability to successfully engage in new tasks and can be divided into three categories: information, mental procedures, and psychomotor (physical) procedures. The taxonomy postulates the three domains of knowledge are operated on by the systems of thought i.e. the hierarchical mental operations of the levels act differently on each of the knowledge domains (Figure 2.1). Knowledge in any subject can be characterized by how much of each of these categories it comprises. The information domain consists of specific information or content knowledge that is represented in the memory in the propositional form (smallest unit of thought that stands as separate assertions) and is divided into two categories: organizing ideas (principles and generalization) and details (vocabulary word, facts, time sequences). Two examples of the

information domain when exploring thermometric titrations include the principles and terminology associated with acid-base chemistry and equations related to enthalpy of a reaction.

Mental procedures (process knowledge) refer to the ability to utilize the knowledge, and ranges from simple tasks such as algorithms to complex processes such as essay-writing. Mental procedures are divided into two categories: skills which can be executed automatically or with little conscious effort after some practice and processes composed of highly complex procedures producing a variety of results that involve carrying out many interrelated subcomponents. Examples of mental procedures are the ability to use acid-base chemistry and enthalpy changes to make volumetric calculations (simple skills) or used to determine the heat of neutralization from titration data (complex processes).

Psychomotor procedures may be simple or complex physical processes required by the subject that vary by subject area and may be learned to be performed automatically. Mental and psychomotor processes must first be learned as declarative knowledge, and then practiced in order to become automatic. The use of a buret in measuring volume of a titrant is an example of a simple psychomotor skill, and determining how the titration equipment would allow for the determination of the endpoint of the thermometric titration would be a complex process. Examples of how each knowledge domain (information, mental procedures and psychomotor procedures) interacts with two mental operations (investigating level in the cognitive system and examining efficacy in the self-thinking system) are handled differently by these operations for thermometric titrations are shown in Table 2.

Table 2.2. Example of mental operations acting on the three knowledge domains as it relates to thermometric titrations.

	Task	Investigating	Examining efficacy
<i>When asked</i>		<i>Student uses</i>	<i>Student identifies and analyses</i>
Information	<i>Organizing ideas</i>	knowledge of sign changes as it relates to enthalpy to investigate the thermometric titrations.	extent of understanding of titrations and enthalpy change can be improved.
Mental	<i>Details</i>	knowledge of neutralization principles to investigate the titration enthalpy changes.	improvements to the understanding of acid-base concepts at the molecular level.
	<i>Processes</i>	understanding of how to manipulate titration data to calculate the heat of neutralization.	how the competence at the manipulation of titration data can be improved.
Mental	<i>Skills</i>	understanding of volumetric calculations to investigate thermometric titration.	competence at how the understanding and drawing titration graphs can be improved.
Psychomotor	<i>Processes</i>	understanding of how to operate titration glassware to gather titration data.	the ability of how the utilization of titration glassware can be improved.
	<i>Skills</i>	understanding of buret use to determine the volume of base needed for neutralization.	how the competence on the use of pipet to dispense the acid into the cup can be improved.

M&K provide a variety of psychological and educational literature-based theory and research to support their theoretical framework (22,27-31). Garcia and Pintrich found that students regulate their efforts as a function of their self-conception, motivation strategies (self-system thinking), and cognitive strategies (28). Harter reported research on the perception of competence in children and found parallels between the teacher's perception of a student's competence and the students' perception (29). Bandura presented a discussion and analysis of self-regulation and its effects on human behavior which demonstrates that self-reflection exercises control over thoughts and motivation (30). Bandura also found that expectations of efficacy determined whether coping behavior will be initiated, how much effort is used, and for how long it will be sustained in the face of obstacles (22). Ajzen et al. reported research that suggests a connection between attitudes and importance to resulting behaviors, where a person's attitude has a strong relation to their behavior for

the same target and the same action (31). Flavell suggests that metacognitive interactions of strategies, knowledge, goals, and experiences have control over cognitive enterprises (cognitive thinking) and suggests increasing the quality and quantity of metacognition. Flavell suggests teaching how to monitor cognition (metacognition) could lead to better learning, and ability to how well a message is understood or should be accepted or rejected (27).

The taxonomy by M&K is based on Bloom's taxonomy of educational objectives and hence contains similarities in its structure and purpose (20). Bloom's taxonomy, named for the main editor, Benjamin Bloom, is the collaboration of a group of educational researchers in attempt to develop a classification of educational objectives (21). The taxonomy is most influential on evaluation rather than curriculum development (20). Bloom's taxonomy is arranged into three domains – cognitive, affective and psychomotor (Table 2.3) (21,38,39). The cognitive domain, the most commonly used portion, consists of objectives that deal with recognition of knowledge and development of intellectual skills and abilities. The affective domain has received much less attention than the cognitive domain and emphasizes emotions, degree of acceptance or rejection, changes in interest and attitudes (20,32). The third domain involves either muscular or motor-skills, manipulation of materials or objects, or neuromuscular coordination. These are most commonly found in handwriting, speech, physical education and technical courses, however this work was not completed by Bloom and his colleagues (20,21,33) but was described by authors such as Harrow (34). Various revisions have been made to the Bloom's taxonomy by authors such as Anderson, Krathwohl and de Kock et al in order to update or improve the initial endeavor (35,36,37).

Table 2.3. Definitions of cognitive and affective Bloom's domains and corresponding levels.

Domains	Levels	Description	Categories and subcategories
Cognition	Knowledge	Retrieve by recall or recognition of information.	Ways and means of dealing with specifics, conventions, trends and sequences, classifications and categories, criteria, methodology, universals and abstractions
	Comprehension	Understand information, grasp terminology, interpretation, extrapolation	Translation, interpretation, extrapolation
	Application	Use concepts, methods, and theories in new circumstances to solve problems	
	Analysis	Separate concepts into parts so that its organizational structure may be understood and distinguishes facts and inferences.	Elements, relationship among elements and organizational principles
	Synthesis	Generate new knowledge structures and putting together elements and parts to form a whole, involves creative behavior.	Unique communications, plan or set of operations and abstract relationships
	Evaluation	Make judgments on value of knowledge and is conscious decision making.	Judgments in terms of internal evidence, and judgments in terms of external criteria

Table 2.3. Definitions of cognitive and affective Bloom’s domains (continued).

Domains	Levels	Description	Categories and subcategories
Affective	Receiving	Receive or attend to phenomena or stimuli	Awareness, willingness to receive, controlled/selected attention
	Responding	Show interest, seek out or engage in an activity or phenomena	Acquiescence in responding, willingness to respond, satisfaction in response
	Valuing	Place worth on a phenomena or behavior	Acceptable of a value, preference for a value, commitment,
	Organizing	Classify or prioritize values	Conceptualization of a value, organization or a value system
	Characterization by a value	Develop value system of behavior	Generalized set, characterization

The cognitive domain in Bloom’s taxonomy is organized into six levels, while the affective domain is classified into five levels. Bloom ascertains that the level of difficulty of a problem is associated with these levels, with higher levels being more complex. These levels were arranged from simple to complex and it was suggested that in order to tackle the successive levels, the preceding levels must be mastered, hence is arranged in a hierarchical format (21). The terminology used in both Bloom and M&K’s taxonomies differ in terms of the classification of knowledge in domains and systems. The cognitive and self-system thinking of M&K have similarities to the cognitive and affective domains of Bloom’s taxonomy respectively. The psychomotor domains of both taxonomies have the same description, but are treated differently. A brief summary of the cognitive and affective domains of the Bloom’s taxonomy is described in Table 2.3 and a comparison of taxonomies is presented in Table 2.4.

Table 2.4. Comparison of the taxonomies of M&K and Bloom.

Bloom's taxonomy		Comparable to levels of M&K's taxonomy
Cognitive	Knowledge	Retrieval
	Comprehension	Comprehension
	Application	Knowledge utilization- problem solving
	Analysis	Matching and generalizing
	Synthesis	Analysis- classifying and generalizing; knowledge utilization- decision making
	Evaluation	Analysis- analysis of errors and generalizing, knowledge utilization - decision making, self-system- examining importance
Affective	Receiving	New task presented is either accepted or rejected
	Responding	Self-system- examining emotional response and motivation
	Valuing	Self-system -examining importance, Metacognition - monitoring clarity
	Organizing	Self-system -examining importance
	Characterization	Self-system- examining motivation, decision to engage metacognition
Psychomotor		Psychomotor

M&K's taxonomy was developed to respond to the inadequacies of and problems with the Bloom's taxonomy and its revisions (Table 2.5). Even though Bloom's taxonomy is one of the most popular and highly influential on educational practice, it has faced various criticisms (40). Bloom's taxonomy expanded the notion of learning to a multidimensional concept, however, the taxonomy often is regarded as oversimplified characteristic levels (40) and research have shown that it does not consistently recognize higher level questions as more difficult (41,42). Bloom's taxonomy and its revisions use the basis of the differentiation among the levels as degrees of complexity between them. Marzano and Kendall use the number of steps and the level of familiarity with the process to differentiate the levels. Their reasoning points to the fact that even complex processes can be learned at a level of little effort and they argue that mental processes can be ordered in terms of control i.e. some processes have control over the operation of others.

Table 2.5. Summary of the problems with Bloom’s taxonomy addressed by M&K.

Problems of Bloom and revisions	How addressed by M&K
Difficulty of material is a result of the cognitive level.	Difficulty results from the complexity of mental processes employed.
Hierarchical nature is based on the complexity of problems	Hierarchical nature based on flow of mental processing
Content and process knowledge are combined as one system.	Knowledge separated into a two dimensional model of knowledge domains and thinking systems.
Affective, cognitive and psychomotor are addressed as one dimensional knowledge.	Affective, cognitive and psychomotor are distinguished as thinking systems and the knowledge domains.
Behaviors are discussed as mental acts or thinking.	Behaviors affected by three systems of thought and objectives focus on these behaviors.
Higher levels of thought (metacognition and self-system) were not addressed.	Metacognition and self-system thinking addressed.
Metacognition and self-system were not discussed as distinct systems.	Metacognition and self-system thought are explained distinctly

The hierarchical structure of Bloom’s taxonomy does not hold together in all circumstances as seen in published research (20). Various researchers have shown that the levels of Bloom’s taxonomy are either not well explained or the levels are confusing. For example, the comprehension and analysis levels are easily exchanged. The evaluation level is not more complex than synthesis in all circumstances, but rather synthesis involves evaluation (40). The authors of the original taxonomy also suggest that the evaluation level may come before other levels allowing students to skip levels depending on the students’ familiarity with the problem. Bloom states “Although Evaluation is placed last in the cognitive domain because it is regarded as requiring to some extent all the other categories of behavior, it is not necessarily the last step in thinking or problem solving. It is quite possible that the evaluative process will in some cases be the prelude to the acquisition of new knowledge...” (2). The hierarchical nature of M&K’s taxonomy is, however, based on the flow of mental processing, rather than on the level of complexity of its specific levels. The self-system first

determines whether knowledge is important enough to learn, after which metacognition is engaged to establish goals relative to the knowledge employing the cognitive processes (1).

The separation of levels of processing and knowledge domains demonstrates the difference between actions and the “object of the actions”. Bloom’s taxonomy mixes mental operations with the knowledge domains they act upon and does not make this distinction even though it is recognized these mental operations are distinct from knowledge (1,40) Anderson, who revised Bloom’s work, suggests that’s content knowledge is factual and conceptual information is typically associated with nouns, while the process knowledge is the cognitive process performed on the knowledge (verb) (35). M&K’s taxonomy separates distinctly that the three domains of knowledge (content knowledge) are operated on by the three systems of thinking (process knowledge) and their mental operations (Figure 1) (1). M&K makes a clearer distinction of the thinking systems as cognitive, metacognitive and self-system thinking relating them to expected behaviors, and the knowledge domains acted upon as psychomotor, mental procedures and information. The new taxonomy includes physical procedures as a type of knowledge as it is believed to be stored in memory and the methods of acquisitions are similar to mental processes (1).

M&K’s taxonomy is based on the model behavior in which a new task is presented to the learner, and the learner has the opportunity to engage and attend to the task leading to a change in behavior (Figure 1). This decision to change the current behavior and its subsequent actions are determined by the interaction by the three systems of thought. Both Anderson and M&K classify educational tasks accounting to the types of knowledge in the instruction and the mental processes that the task imposes on the knowledge, where the objectives focus on the behaviors to be developed and the content that the behavior operates on (1,35).

Higher levels of thought (self-system thinking and metacognition) are not addressed by Bloom’s taxonomy. Revisions to Bloom’s taxonomy suggest more than one form of knowledge or

classify Bloom's levels as one cognitive level, suggesting higher levels of thinking (35,36,43). Krathwohl and Pintrich (revisions to Bloom) suggest two-dimensional knowledge that includes metacognition as content knowledge, rationalizing its importance as the "knowledge of cognition and the processes involving the monitoring, control, and regulation of cognition" (36,43). Anderson's metacognitive knowledge level appears in the knowledge dimension as the information used by the cognitive level and is placed sequentially *after* the cognitive level (35). M&K suggest that goals are established by the metacognitive system and explicit or not can affect the type of cognitive processes that occur. Therefore metacognition represents a type of processing rather than the knowledge dimension and is placed before the cognitive system. The placement of metacognition in M&K is different from these revisions as it is placed above the cognitive processes and not as a knowledge domain as in these revisions (35,36). M&K's taxonomy includes the self-system thinking, which is placed sequentially above the metacognitive system (20). A clear distinction between self-system and metacognition is made by M&K, as it is shown that self-system to an extent determines the functioning of the other two systems (24,44). Self-system thinking controls whether the learner decides to engage in a new task or not. The revised taxonomies, however, include self-system as part of metacognitive knowledge.

The M&K taxonomy was used for the development of educational objectives for instruction and assessment tools. In order to develop the objectives, three criteria must be met (20,45). Instructional objectives must include 3 aspects of the expected performance: a) what is expected of the learner, b) results or products of the performance and c) conditions necessary for the performance to occur. Lastly, if possible, the criteria by which the performance of the learner is considered acceptable. M&K, like Bloom and Anderson, write the educational objectives beginning with "The students (or students) will be able to". M&K follow this phrase with a mental operation (verb) and then the object or knowledge it acts on. They state also that many of the elements of the

metacognitive and self-system thinking levels may seem beyond the responsibility of the school or teachers when building objectives. All material may not be important enough to be covered at every level of the taxonomy, but M&K have presented supporting research suggesting the inclusions of metacognitive and self-system thinking objectives where possible particularly if self-regulatory skills are to be developed (20).

Assessments defined by M&K are “methods of gathering information about the students’ achievement or behavior” and evaluations are “making judgments about the level of students’ understanding or performance”. Various assessment tools may be used such as forced-choice (multiple choice), performance tasks, written reports, graphic organizers (concept maps), charts, graphs, pictographs and teacher observations. Performance tasks are assessments which require students to construct their own responses and apply knowledge. Teacher observations are collected informally through the observation of the students over a short period of time. The complexity of tasks or questions is based on additional steps required of a question or unfamiliarity of material, rather than from a level of the taxonomy.

Various reasons were employed when deciding on a framework for the educational objectives and assessments for the sensorial experiments. The taxonomy by M&K is a current model (2007), but is based on one of the most popular and commonly accepted taxonomies (Bloom). The M&K taxonomy has been developed over several years using numerous psychological and educational theories and research. The taxonomy deals with the problems of the Bloom’s taxonomy and the revisions addressed in the literature. It incorporates objectives that propose change in students’ behavior which would encourage critical thinking skills necessary in learning labs, rather than just the development of cognitive processes. The taxonomy demonstrates a two dimensional model of learning, for which students utilize various forms of knowledge (content, procedural and psychomotor) with in different thinking systems.

2.3 Learning Lab Report format

Scientists engage in and learn science through inquiry, which strongly supports teaching science in the classroom through an inquiry process. Research has shown that asking directed laboratory questions and promoting inquiry improves students' performance as shown in the Science Writing Heuristic (SWH) approach by Greenbowe et al. (46). In addition, SWH is designed to facilitate science learning from laboratory experiments to produce meaningful writing construction (47). This format is different from traditional recipe-like formats in which students simply follow directions to verify an already known conclusion. SWH provides students with a guideline for writing lab reports, rather having students use the data to merely fill-in-the blanks or answer multiple choice questions about the data (48). It consists of a template to aid the design of inquiry activities and a template to assist students in their thinking and writing. The SWH approach involves exploring initial ideas about the concept, collaborative inquiry activities and making conclusions through reflection on experimental data, where the instructor actively guides students to develop conceptual understanding.

While the SWH focuses on improving the students' scientific writing, the Model–Observe–Reflect–Explain (MORE) model centers on students' reflection on the concept as it relates to the experiment. The MORE thinking frame guides students' thinking, making them aware of their ideas and prompting students to revise their ideas in light of experimental evidence (49). In this model, students present their initial understanding of the concept by verbally and pictorially depicting the concepts (model), conducting experimentation (observe) and considering the observations as these relate to the concepts and their initial ideas (reflect and explain). This model allows for students' understanding of the concepts to progress towards being acceptable by refinement of ideas.

We have developed the Learning Lab report, LLR, in our research group as another alternative model for traditional laboratory report, with the goal of transforming the traditional

reports into something more useful for *both* students and instructors (Table 1). The LLR assessments were fashioned using theoretical framework of Marzano and Kendall (M&K) (45) and utilizes conceptual questions to enhance students' thoughts in developing their discussion, conclusion and reflection sections. Conceptual questions involve students constructing answers rather than simply recalling information or use algorithms. Conceptual questions can evoke answers of higher cognitive thinking such as metacognition thinking, knowledge utilization and analysis skills. The use of conceptual questions a tool that can aid students in gaining a greater learning experience by improving their conceptual understanding, develop the ability to apply concepts to new situations and develop their critical thinking skills. Conceptual questions involve students constructing their answers and use an understanding of the concept to find a solution to a problem, rather than just recalling experimental procedures and details. This is in contrast to an algorithmic problem, which can be solved using a memorized procedures or principles (50).

The LLR focuses primarily on reflection of initial thoughts and experimental data to promote both the students self-system learning and metacognitive skills (51). The LLR benefits students by organizing their lab report in a scientific inquiry format (Table 2.6) with the goal of maximizing their learning process by sequentially progressing to an acceptable conceptual understanding of the experiment. The LLR allows students to gain a constructive inquiry experience from the laboratory and develop their lab report writing through a structured format. This design provides a detailed format for lab writing construction by clearly delineating the lab report sections such as the results, discussion, conclusion and reflection sections and includes conceptual questions to enhance students' thoughts in these different sections. These conceptual questions focus on the macroscopic, particle and symbolic representation of matter to explore students' visualization of chemistry concepts. The LLR also allows *instructors* to monitor students' thought processes from the pre-lab to post lab using these conceptual questions. Students' pre-lab responses, experimental routes chosen, reflections and

responses to conceptual questions demonstrate students' thought processes throughout the lab experiment, allowing instructors to monitor these thought processes sequentially.

Table 2.6. Basic structure of the Learning Lab Report.

Learning Lab	Composition	Scientific Inquiry
1. Pre-thoughts	Pre-lab inquiry questions	Develop ideas/ hypothesis
2. Method	Prewritten experimental details	Experiment/method
3. Results and Discussion	Data collection, data analysis and probing questions	Data collection and analysis
4. Conclusions	Make generalizations about concept	Draw conclusions
5. Reflection	Re-think pre-thoughts and reflection on concept as it relates to the lab	Re-develop hypothesis, re-evaluate ideas
6. Team Work	Evaluation of collaborative skills	Collaborative efforts evaluated

The LLR promotes scientific inquiry in the laboratory and aims to encourage students' critical thinking skills through directed questions. Pickering suggests that a lab should not merely teach concepts or aim to master skills, but teach students how to think with respect to data, hence the need to use the scientific method (52). The LLR centers on these questions to promote reflective thinking, where students consider their initial thoughts and experimental data to enhance learning through the creation of new ideas during the laboratory (46). The LLR format is similar to the scientific inquiry process and used conceptual questions to guide students in proposing or developing ideas about the concept (pre-thoughts), devising a means of collecting data to explore the concept (method), interpreting the data collected (results), summarizing results (discussion), drawing conclusions and re-developing initial ideas (reflection) (Table 1). The LLR focuses on students' thoughts and reflective thinking in order to allow instructors to observe their learning process. Learning is enhanced by "critical reflection" and involves the "creation of meaning and conceptualization from experience" (52). The LLR uses conceptual questions to guide students in evaluating concepts before performing the laboratory experiment (pre-thoughts), then re-organize and reconstruct their own knowledge based on their laboratory data (conclusions and reflection). The LLR also asks students to evaluate their performance in the lab, as well as the performance of their

group to get students to reflect on the effectiveness of their efforts and the areas they can improve on. This also allows the instructor to evaluate the students learning experience in the laboratory and modify their teaching materials and instructional strategies. The instructor is able to then take action during the process in order to facilitate establishing relationships between the concepts and experimental data. However, any intervention or action taken is done without revealing the answers to the assignment to maintain an inquiry approach. Hence, the information obtained from these reports can also serve to guide the instructor in their teaching.

The LLR approach has similar characteristics to the SWH and MORE formats in that they all engage students through collaborative inquiry, utilize reflective thinking to make conclusions about the concept and emphasize meaningful writing construction (Table 2). These aspects are enhanced in the LLR, as the reflection process is not limited to drawing conclusions (SWH) or re-thinking initial thoughts (MORE), but incorporates both of these types of reflection through the use of conceptual questions in addition to reflection of the students ideas on their performance and the performance of their group (metacognition and self-system thinking). The LLR provides an outline for students in developing a meaningful laboratory experience through conceptual questions. The format approach uses this concept testing to aid meaningful discussions, conclusions about the experiment, reflection on the concept and guide students' lab writing construction.

The LLR is initiated so that students provide their initial thoughts and ideas about the concept under investigation (with inquiry-promoting pre-lab questions). These pre-lab questions are structured to allow students to think ahead about definitions, calculations, simple applications, and comparisons between relevant topics. These questions primarily evaluate students' retrieval level (lowest cognitive thinking system) and are also used to identify students' misconceptions, beliefs on their knowledge and thinking processes related to the topic under investigation (self-system thinking). Students must write a method or procedure for the inquiry experiment in their own words,

where they must either devise their own experimental route with minimal guidelines or re-write the given procedure incorporating additional information relevant to the experiment making it more useful to the student during the lab (metacognition). This promotes preparation practices as they must read the experimental procedure or guidelines before the laboratory and consider what additional information they may need to perform the experiment. Their procedure should state the concept they will be exploring and the experimental route necessary to collect data.

Students present their results in a logical and useful format such as tables or graphs with detailed observations. Guidelines or suggestions on data collection methods may be given to allow for uniformity or completeness in their data collection, but these should not limit students' creativity. Students are asked to use their data to make inferences about the concepts and prompting questions are used to aid students' data analysis utilizing mid-level cognitive thinking skills. Students contemplate their results with directed questions and use this information to analyze new situations. Students may also use this opportunity to evaluate their original ideas and rationalize or correct their answers with the evidence collected.

We have developed the LLR to promote higher level cognitive thinking by critical analysis of the data, utilizing the knowledge gained during the experiment (cognition), determining the clarity of the knowledge gained (metacognition), examining their beliefs and rationalize the importance of the concept (self-system). Students derive definitions and generalizations to draw conclusions about the investigated concept with the use of directed questions (analysis). Students devise a plausible question and answer to the question about the experiment, which requires them to utilize their knowledge of the concept (knowledge utilization). Students demonstrate their reflective thinking through the development of their own questions in the post lab report, which can be used as an indicator of a quality learning experience (the ability to develop and stimulate students' conceptual understanding) (53). They also make comparisons between aspects of 'everyday life' and the

chemical concepts explored by identifying important similarities between concepts (examine importance and beliefs about the concepts). After the Learning Lab report is handed in, students evaluate their own lab performance as well as the collaborative efforts of their group (metacognition and self-thinking). They may freely express whether their group helped their understanding and state the groups' efforts towards the experiment or problems in the group. Instructors may monitor students' interactions in the groups and evaluate whether students recognize the importance of collaborative work.

Application of M&K and LLR to the Sensorial Experiments

The design of the sensorial experiments and learning lab reports align with the M&K taxonomy. Examples of the conceptual questions used in the LLR are presented with each experiment in Chapter 3 and the entire LLR for each experiment are presented in the Appendices. The sensorial experiments are designed to be inquiry in nature in which the students must plan the route of their experimentation or through investigative questions analyze experimental results. Students must first engage their self-system thinking in deciding the importance of the material and their motivations for proceeding. The use of multiple or different senses in the sensorial experiments may promote diverse learning environments (particularly visual, audio and tactile) and potentially be reflected in the students' attitudes, motivation and perspectives on the experiment. Students interest in the sensorial experiments may be engaged by the novelty of using multiple or different senses in making chemical determinations. This is reflected in some of the conclusions and comments on the post lab reports such as in the Qualitative organic analysis experiment where some students related the significance of olfaction in making classifications (see Chapter 3 section 3.2). The use of direct self-reflective questions is utilized to encourage students' self-system thinking as it relates to the experiment, rather than simply assessing cognitive system thinking.

Students must engage the metacognitive thinking in order develop strategies for developing their experimentation or developing an analysis for the experiment. Metacognition is a skill that M&K suggest can be taught by providing guidelines such as asking students what is necessary in setting goals (resources, plans, skills needed etc.). The methods used in the sensorial experiments to encourage the metacognitive system in addition to lower level cognition include requiring:

- a) experimental plans.
- b) how students' experimental methods may or can change depending on a situation.
- c) asking about resources or concepts needed.
- d) students' technique for answering questions or making calculations.
- e) what information or skill is necessary to complete a task or calculation.

Students are asked to either devise experimental plans or make comparisons to a given experimental route of other methods such as comparing thermometric titrations to colorimetric titrations. Students may be required to decide what chemicals or conditions are required for an experiment or what other conditions could be used to perform the same experiment. All metacognitive tasks do, however, require some level of cognitive thinking to make decisions about their goals, the effectiveness of the procedures and monitoring their understanding.

The engagement of the metacognition allows students to make decisions about cognitive processes necessary to develop experimental routes, analyze experimental data, make conclusions and apply the information to new situations. The questions are developed to promote all cognitive skills in order for students to analyze data and answer directed questions in the post lab. They are faced with the different types of information (knowledge domains) in the experiment. They must be able to exhibit declarative knowledge giving details, vocabulary and facts about the concepts explored. Students must be able to know how the information is to be used in calculations and construction of graphs (mental procedures). The experiments require the use of glassware,

instrumentation and apparatus for which students must have a working knowledge of how to use and manipulate in the lab (psychomotor procedure). Various assessments tools may be employed to evaluate the cognitive thinking of students as described previously.

The learning labs are designed to use reflective thinking to improve critical thinking skills and require introspection of the students' thoughts, attitudes, and motivations (self-system thinking). Critical thinking is a result of reflecting on learning and 'ability to reflect on thoughts, feelings and actions' (self-system) (46). The format of the learning labs aligns with the hierarchy of the taxonomy where the pre-lab questions require mostly the lower levels of cognition such as retrieval while the conclusions require primarily knowledge utilization. Students are given pre-lab questions which are used to primarily assess students understanding at the lower cognitive levels and focuses on declarative knowledge and simple skills (mental procedures). Students are given an opportunity to review their pre-lab responses after performing the laboratory. They are asked specifically to reflect upon the questions and discuss any changes in their thoughts, beliefs and emotions as these pertain to the questions. Students must then make judgments about their knowledge, decide on new goals, state processes needed to analyze the data and determine their clarity on the information (how clearly they understand the material) after performing the experiment.

The in-lab activities require students to use procedural knowledge to perform the experiment. Students analyze their resulting data using mid-level cognitive skills applying them to simple and complex procedural knowledge. The post-lab questions require comprehension, analysis and knowledge utilization of the observations and results of the experiment, along with information from the related course material. Students draw meaningful conclusions about the experiment with directed questions demonstrating knowledge utilization and analysis skills. Knowledge utilization is required for students to make connections to real world applications and develop a question related to the experiment.

The sensorial experiments developed have all utilized the chemical and pedagogical objectives discussed. Experiments were rigorously tested in our laboratory before implementation. All experiments except the olfactory titration were implemented in the undergraduate laboratories. The pedagogical objectives of these experiments are based primarily on the taxonomy of educational objectives of Marzano and Kendall (M&K) (20). The Learning Lab Report (LLR) format was developed as a comprehensive laboratory format and used with the equilibrium, titration and acetyl salicylic acid experiments. Since the LLR was used only for these experiments, a discussion of the common misconceptions and relevant literature and implemented interventions are also discussed. From the results of the LLR, all experiments were reviewed and re-written to address any learning problems. The final revised experimental procedures, pre-lab and post lab reports with instructor's notes have been included in the appendices. The discussion of the sensorial experiments includes an overview, results of the implementations, pedagogical and chemicals challenges.

REFERENCES

1. Santangelo, V., Spence, C. *J. Exp. Psychology: Human Percep. Perform.*, **2007**, *33*, 1311–1321.; Moats, L. C., Farrell, M. L., Multisensory Instruction In *Multisensory teaching of basic language skills*, Birsh, J. R. Paul H. Brookes Publishing Co., MA, 2000. Chapter 1.
2. Wood, C. G. *J. Chem. Edu.* **1990**, *67*, 596.
3. Goodwin, T. E. *J. Chem. Edu.* **2004**, *81*, 1187-1190.
4. Nakhleh, M. *J. Chem. Educ.* **1992**, *69*, 191-196.; Taber, K. S. *Chemical misconceptions - prevention, diagnosis and cure, L: Volume 2*, London: Royal Society of Chemistry; 2002.
5. Bodner, G. M. *J. Chem. Edu.* **1986**, *63*, 873.
6. Jarvis, T.; Hargreaves, L.; Comber, C. *Res. Sci. Educ.*, **1997**, *27*, 223-236.; Sood, K. *Quality Science Investigation in the Early Years*, Report in Childhood Education: International Perspectives, pp 2-12, 1996., Ross, M. R.; Fulton, R. B. *J. Chem. Edu.* **1994**, *71*, 141-143.
7. Herman, C. *J. Chem. Edu.* **1998**, *75*, 70-72.
8. Domin, D. S. *J. Chem. Edu.* **1999**, *76*, 543-547.
9. Mohrig, J. R., Hammond, C. N., Colby, D. A. *J. Chem. Edu.* **2007**, *84*, 992-998.
10. Rosenberg, R. E. *J. Chem. Edu.* **2007**, *84*, 1474-1476.
11. Bopegedera, A. M. R. P. *J. Chem. Edu.* **2007**, *84*, 465-468.
12. Cacciatore, K. L.; Sevian, H. *J. Chem. Edu.* **2006**, *83*, 1039.
13. Cacciatore, K. L.; Sevian, H. *J. Chem. Educ.* **2009**, *86*, 498-505.
14. Taylor, T.E. *J. Coll. Sci. Teach.* **1976**, *5*, 320.
15. Cooper, M.M. *J. Chem. Edu.* **1995**, *72*, 162.
16. Adams, D.; Hamm, M.; *Collaborative Inquiry in Science, Math, and Technology*, Chapter 1, Heinemann, New Hampshire, 1998.
17. Giancarlo, L. C., Slunt, K. M. *J. Chem. Edu.* **2004** *81* 868.
18. Tribe, L., Kostka, K. *J. Chem. Edu.* **2007**, *84*, 1031.
19. Cracolice, M. S. *How Students Learn: Knowledge Constructions in College Chemistry*, Eds. Pienta, N. J., Cooper, M. M., Greenbowe, T. J. Chapter 2, in *Chemists' guide to effective teaching*, Pearson Education Inc., NJ, 2005.

20. Marzano, R.J., Kendall, J.S. *The New Taxonomy of Educational Objectives*, 2nd Ed. 2007, Corwin Press, California.
21. Bloom, B. S., Engelhart, M. D., Furst, E. J., Hill, W. H., Krathwohl, D. R. *Taxonomy of Educational Objectives, The classification goals Handbook I: Cognitive Domain*, 1964, David McKay Company Inc, New York.
22. Bandura, A. *Psychological Review*, **1997**, *84*, 191-215.
23. Malmivuori, M. *Educational Studies in Mathematics*, **2006**, *63*, 149-164.
24. Bandura, A. *Educational Psychologist*, **1993**, *28*, 117.; Bandura, A. *Self-efficacy*. 1994, www.emory.edu/EDUCATION/mfp/BanEncy.html. (accessed July 2008).
25. Posner, G. J.; Strike, K. A.; Hewson, P. W.; Gertzog, W. A. *Science Education*, **1982**, *66*, 211–227.
26. Bandura, A. *American Psychologist*, **1989**, *44*, 1175-1184.
27. Flavell, J. *American Psychologist*, **1979**, *34*, 906-911.
28. Garcia, T., Pintrich, P. R. *Self-Schemas, Motivational Strategies and Self-Regulated Learning*, Presented at the Annual American Educational Research Association Meeting, Atlanta, 1993.
29. Harter, S. *Child Development*, **1982**, *53*, 87-97.
30. Bandura, A. *Organizational Behavior and Human Decision Processes*, **1991**, *50*, 248-287.
31. Ajzen, I., Fishbein, M. *Psychological Bulletin*, **1977**, *84*, 888-918.; Ajzen, I., Madden, T. J. *Journal of Experimental Social Psychology*, **1986**, *22*, 453-474.
32. Krathwohl, D. R., Bloom, B. S., Masia, B. B. *Taxonomy of Educational Objectives, The classification goals Handbook II: Affective Domain*, 1964, David McKay Company Inc, New York.
33. Atherton, J. S. 2005 *Learning and Teaching: Bloom's taxonomy*, UK: <http://www.learningandteaching.info/learning/bloomtax.htm> (accessed: October 2008).
34. Harrow, A. *A taxonomy of psychomotor domain: a guide for developing behavioral objectives*. New York: David McKay, 1972.
35. Anderson, L. W., Krathwohl, D. R., Aiasian, P. W., Cruikshank, K. A., Mayer, R. E., Pintrich, P. R., Raths, J., Wittock, M. C. *A Taxonomy for Learning, Teaching, and Assessing: A Revision of Bloom's Taxonomy of Educational Objectives*. 2001, Addison Wesley Longman, Inc; Anderson, L. W. **1999**, Report, US Department of Education.
36. Krathwohl, D. R. *Theory into Practice*, **2002**, *41*, 212-218.

37. de Kock, A., Slegers, P., Voeten, M. J. M. *Review of Educational Research*, 2004, 74, 141-170.
38. Pungente, M. D., Badger, R. A. *J. Chem. Edu.* **2003**, 80, 779.
39. Clark, D. R., Last updated June 2007, Learning Domains or Bloom's Taxonomy, <http://www.nwlink.com/~donclark/hrd/bloom.html>; (accessed 6th August 2008).
40. Kreitzer, A.E., Madaus, G. F. 1994, Empirical Investigations of the Hierarchical Structure of the Taxonomy in Anderson, L. W., Sosniak, L. A.(eds.) Bloom's Taxonomy: A Forty-Year Retrospective, University of Chicago Press, Chicago, Illinois.
41. Furst, E.J. *Review of Educational Research*, **1981**, 51, 441-453.
42. Poole, R. L. *Psychology in Schools*, **1972**, 9, 83-88.
43. Pintrich, P. R. *Theory into Practice*, **2002**, 41, 219-225.
44. Rouxel, G. *Learning and Individual Differences*, **2000**, 12, 287-310.; Pintrich, P. R., DeGroot, E. V. *Journal of Educational Psychology*, **1990**, 82, 33-40. Pajares, F., Graham, L. *Contemporary Educational Psychology*, **1999**, 24, 124-139.
45. Marzano, R.J., Kendall, J.S. *Designing & Assessing of Educational Objectives: Applying the New Taxonomy*, 2008, Corwin Press, California.
46. Lerch, C., Bilics, A., Colley, B. Using Reflection to Develop Higher Order Processes, Annual Meeting of the American Education Research Association, 2006.
47. Wink, D. J.; Hwang-Choe, J. H. *J. Chem. Edu.* **2008**, 85, 396-398.
48. Rudd, J. A., II; Greenbowe, T. J.; Hand, B. M. *J. Chem. Edu.* **2007**, 84, 2007-2011.; Pooch, J. R.; Burke, K. A.; Greenbowe, T. J.; Hand, B. M. *J. Chem. Edu.* **2007**, 84, 1371-1379.; Burke, K. A.; Greenbowe, T. J.; Hand, B. M. *J. Chem. Edu.* **2006**, 83 1032-1038.; Rudd, J. A., II; Greenbowe, T. J.; Hand, B. M.; Legg, M. J. *J. Chem. Edu.* **2001**, 78 1680-1686.
49. Worrell, J. H. *LabTrek: Experiments for General Chemistry*, 3rd ed., Contemporary Publishing Co., NC, 1997; Aukszi, B. *General Chemistry 2 Laboratory*, 2nd ed., Outernet Publishing, LLC, MN, 2004.; Levine, S. L. *Laboratory Manual for Chemistry 102*, Pearson Custom Publishing, 2002..
50. Cracolice, M. S.; Deming, J. C.; Ehlert, B. *J. Chem. Educ.* **2008**, 85, 873.
51. Mattox, A.C.; Reisner, B. A.; Rickey, D. *J. Chem. Edu.* **2006** 83, 622-624.; Tien, L. T.; Teichert, M. A.; Rickey, D. *J. Chem. Edu.* **2007**, 84, 175-181.
52. Pickering, M. *J. Chem. Edu.* **1985**, 62, 874-845.
53. Teixeira -Dias, J. J.C.; Pedrosa de Jesús, H.; Neri de Souza, F.; Watts, M. *Intern. J. Sci. Educ.*, **2005**, 27, 1123-1137.

CHAPTER 3 . The Sensorial Experiments

3.1 The Sensorial Experiments

A variety of experiments have been researched and concepts from traditional experiments explored including the topics of equilibrium, qualitative analysis, titrations and kinetics for their effectiveness as sensorial experiments. Although the use of instrumentation in chemistry laboratories is sometimes unavoidable, the use of multi-sensory techniques instead of analysis and verifications using these instruments may be beneficial for students (1). Multi-sensory experiments provide a way to promote a diverse learning environment (102,101), encourage learning due to increased sensory attention (95) and improve memory performance because of increased engagement (97) as described in Section 1.4. The experiments implemented into the general and organic chemistry teaching laboratories are a qualitative organic analysis, esterification kinetics study, Le Chatelier experiment, acids-base and redox thermometric titrations and acetyl salicylic acid hydrolysis experiments. An olfactory titration using the smell of the rutabaga vegetable have been developed, but not implemented. These experiments give new learning opportunities for students, as the experiments utilized multiple senses to explore the chemistry topics and at the same time used conceptual questions to guide students in evaluating concepts, allowing instructors to monitor students' changes in their conceptual knowledge.

The development of conceptual questions that promoted reflection was utilized in the organic qualitative analysis and esterification kinetics experiments. These questions assisted the instructors in gauging the students understanding of the experiment and results as the conceptual questions require students to not simply recall information but to provide meaningly responses. The conceptual questions were developed to evoke answers of higher cognitive thinking (metacognition, knowledge utilization and analysis). These questions aimed to improve students' conceptual

understanding and evaluate students' application of the concepts to new situations. The development of these questions and the observation of students' inadequately constructed lab reports led into the development of the LLR. The LLR used conceptual questions to enhance students' thoughts in developing focus in their lab reports, from the pre-lab to the post-lab discussion, conclusion and reflection. The LLR was utilized for the equilibrium, titration and kinetics experiments. The LLR pre-lab questions were given to the students at least a week prior to the experiment, so that the responses could be reviewed, graded and returned prior to the experiment. Students were required to review their responses to the pre-lab which were then re-graded as part of their post-lab report. In order to give students adequate time to reflect on the concepts with relation to their data, students were given at least a week to complete the post-lab report which included the re-evaluation of the pre-lab responses.

Various questioning methods structured around the Marzano and Kendall theoretical framework were used including word associations (6,7), drawing comparisons (compare and contrast) and pictorial representations of molecular and macroscopic levels (7,8). Word associations were used for students to derive information from a scheme or to develop a scheme showing associations between concepts (comprehension and analysis). Comparison questions required students to understand the differences and similarities of various concepts, the goal of which was to promote critical thinking (analysis). Students were asked to make pictorial representations of various concepts as well as answer pictorial conceptual questions (comprehension and knowledge utilization). The conceptual questions allowed the instructors to observe misconceptions and other learning difficulties.

The development (based on the goals in Chapter 2) and implementation of these sensorial experiments and the LLR will be discussed in this chapter. Specific challenges of each experiment, in addition to the pedagogical and chemical objectives outlined in Chapter 2, are explored in detail in

relation to safety issues, planning and execution, and the development of LLR objectives (where applicable). Research into specific learning difficulties and misconceptions are discussed along with the appropriate interventions. All experimental hazards and precautions have been evaluated for each experiment. This information is available in the appendices as well as students' experimental protocols, rubrics, intervention activities and instructor's notes. Suggestions for future implementation of the sensorial experiments and LLR are explored briefly with each experiment in this chapter.

3.2 Qualitative Organic Analysis Experiment

Qualitative organic analysis is the recognition of organic functional group(s) in a compound via chemical tests and/or instrumentation. In traditional qualitative organic analysis experiments students may be given a specific unknown to identify by chemical tests and verify their results by confirmatory techniques (chemical tests or spectroscopic techniques). Chemical tests typically involve color changes or precipitate formation in order to determine the functional groups present. Functional groups are commonly identified with the use of instrumentation. Different approaches at qualitative organic analysis show a wide range of tools used by students such as: IR, MS, NMR spectroscopy methods and chromatography to identify unknown compounds (9), computer simulations to discover and prepare a strategy for identifying an organic compound in the laboratory (10,11), flow charts that provide chemical tests based on the solubility of the unknown (12) and a combination of physical properties, classification tests and spectroscopic methods used to determine the functional groups (13). Goller and Miller developed a microscale chemical classification experiment to resolve uncertainties created by unexpected or ambiguous spectral data when separating a mixture containing two compounds (14).

Some studies have demonstrated the effects of structure (functional groups) on the aroma of compounds and found that various functional groups can be identified by aroma (18). Few resources have been found that incorporate the sense of smell into the experiments. A NMR experiment by Uffelman et al. involved the exploration of organic stereochemistry via hands-on model building, chemosensory smell tests, and use of ^{13}C NMR to give students basic knowledge of the instrumentation (15). Students were able to distinguish constitutional isomers (1-butanol, 2-butanol and diethyl ether) and enantiomers (*R*-carvone and *S*-carvone) by smell and acquired a ^{13}C NMR of one of the compounds. An organic experiment utilized aroma to classify various functional groups such as ethers, alcohols and amines to allow students to recognize five aroma classifications (16). Unlike our qualitative organic analysis experiment, their experiment was restricted to alcohols where the identity of the alcohols were provided, therefore the study did not focus on the identification of functional groups or drawing conclusions from the aromas observed.

Some functional groups impart characteristic odors (similar odors) to some of its members and the sense of smell can be a powerful tool in identifying the functional group to which an unknown belongs (17). Studies have shown that people are able to recall with greater accuracy odors over longer periods of time compared to events that are seen (19). These facts were exploited to develop a qualitative organic analysis experiment that would allow students to creatively describe compounds and to remember the functional groups by descriptive aromas. These aroma characteristics would then be used to identify an unknown and multi-sensory confirmatory chemical testing used to confirm the identity of the functional group present in the compound. To develop this experiment, a variety of objectives and considerations had to be achieved which included:

- a) Selection of appropriate compounds.
- b) Confirmatory chemical testing to allow for multi-sensory observations.
- c) Safety and practical issues related to multiple sensory determinations.
- d) Development of questions to probe students' understanding of the experiment.

a) Selection of compounds: The compounds were chosen based on the following criteria:

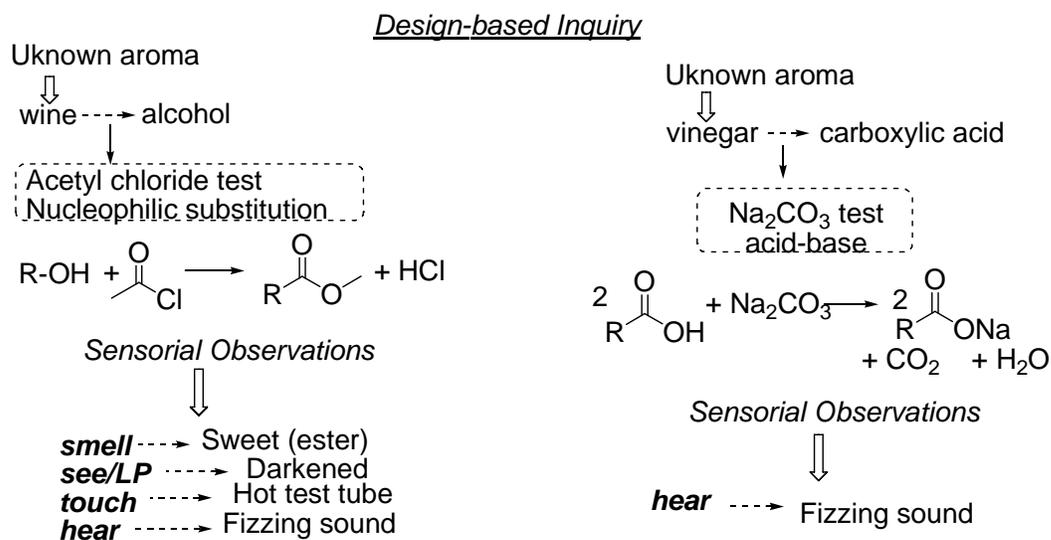
i) familiarity to students, ii) similarity of the compounds by smell and structure so they can be representative of a group, and iii) quality of the aroma produced. The most commonly discussed functional groups in undergraduate organic experiments (10-13) were selected: alcohols, aldehydes, ketones, carboxylic acids, amines, thiols, alkenes and amides. The chemicals chosen were small organic molecules that would represent the selected functional groups and easily be recognizable such as aromas from common household chemicals, foods, medicines, or others that students encounter in their daily lives (Table 3.1). The odor classifications in the Material Safety Data Sheets (MSDS) and fragrance companies (20) were used to establish a list of the reported characteristic aromas of these compounds. Additional compounds without reported odors but with similar structures to those already determined were also selected. To establish which of these compounds would be effective in this endeavor, the compounds were screened for suitability and feasibility for use with undergraduates (strength of aroma). Table 3.1 depicts the functional group aromas found in the MSDS and observed in the laboratory. In addition, aroma quality was considered so that compounds with obnoxious or overwhelming odors were avoided or diluted to minimize these characteristics. For instance, thiols and aldehydes have strong aromas, but were diluted significantly to retain the characteristic aroma, yet prevent the aroma from being overwhelming when wafting.

Table 3.1. Reported aroma descriptions and aromas observed in the laboratory.

Functional Group	Reported Aromas	Odors Observed	Compounds
Alcohol	Mild, rather pleasant, like wine; alcohol like	Rubbing alcohol, wine	Methanol, Ethanol, Butanol, Propanol
Amide	Mousy odor	Wet dog, animal-like	Ethanamide, N-methylacetamide
Aldehyde	New house smell, sharp, aldehyde like, pungent	Preservative, embalming fluid, histology lab	Formaldehyde, butyraldehyde
Ketone	Sweet, nail polish remover, ethereal	Paint thinner, minty sweet	Cyclohexanone, Acetone
Carboxylic Acid	Vinegar, sour, sharp	Vinegar, citrus	Acetic Acid, Citric acid
Amine	Ammonia like, sharp, irritating, fishy, meaty	Ammonia like, fishy	Butyl amine, Diethyl amine
Thiol	Skunk-like, acrid, onion, garlic-like	Burnt rubber, cabbage	Butanethiol, Octanethiol
Alkene	Oil, oil refinery, like	Gasoline, oil	Hexene, cyclohexene
Ester	Fruity, sweet, perfume, pineapple, anise, celery	Fruity, pineapple	Ethyl acetate, n-Propyl acetate

b) Confirmatory testing: The confirmatory tests chosen produced distinct color, clarity, temperature, aroma, and/or sound changes (9,13,21), which were monitored by vision, touch, olfaction, and hearing (Scheme 3.1). The chemical tests used in this experiment are typical organic reactions such as nucleophilic substitutions and oxidations (22) and the expected reactions and possible side reactions which occur with the specific functional group gave products with different physical characteristics from the starting material. The results of these reactions must match *all* the sensory changes expected in order to be a positive confirmatory result. These reactions produced changes in aromas, distinct color changes and precipitate formation, significant temperature changes, ‘popping’ or ‘fizzing sounds’ as illustrated in Scheme 3.1. The examples shown reflect the methods employed: i) examination of non-traditional observations by investigating *all* the resulting products of the reaction, and ii) replacement of chemicals to provide multiple sensory outcomes by considering alternative reactions. For example, the traditional observation given for the acetyl chloride test is the evolution of $\text{HCl}_{(g)}$ and heat. However, other observations that can be made are

the aroma change from alcoholic to ester-like and the color change from clear to dark purple. NaOH was replaced with Na₂CO₃ to produce a fizzing sound with carboxylic acids (Scheme 3.1). The sensory results of each of these tests were unique to the functional group, where all sensory observations collectively created the distinction between the groups. For students unable to view changes in color intensity or clarity, a light probe may be used. A light probe is a device that can distinguish certain visual changes by detecting changes in light passing through the test tube as it emits different frequencies or sound when there are changes in color or clarity of the solution (Figure 3.1).



Scheme 3.1. Sample chemical tests and expected results for alcohol and carboxylic acid.



Figure 3.1. Lumitest light probe.

c) Safety and practical issues: Some practical considerations were taken into account when developing this experiment. Given that the experiment involves observing a variety of functional groups by aroma, the students may quickly become overwhelmed and the laboratory environment itself may become saturated with the aromas. General laboratory procedures would not be sufficient

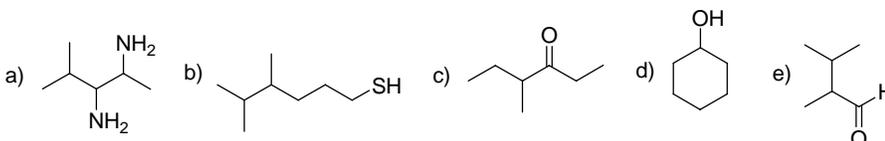
to address these issues and typical practices exhibited by students in the laboratory such as leaving bottles open and incorrect disposal of waste may lead to problems. Students were taught to waft, however, this practice had to be made compulsory to prevent the temptation of directly observing aromas. A modification to the wafting technique was the use of strips of filter paper as smelling strips, similar to those provided in the mall for smelling perfumes. Students added a drop of each chemical on a different strip and ‘fanned’ this aroma towards themselves. Dropper bottles were vital in preventing students from dipping the strips into the chemicals and directly smelling the compounds from the bottles. Smelling strips were also a good way to decrease the potency of the compounds as only a small amount of the chemicals (1 drop of each) was used. Smelling strips were then collected in the hood or in air tight containers for disposal. Another method to reduce odor fatigue was the availability of coffee crystals, a recommended procedure to “clean” the sense of smell. The hazards (MSDS data) of the chemicals used in this experiment were evaluated for short term and long term exposure by inhalation and contact with the skin to determine its suitability for use in the undergraduate labs. Short term exposure to the chemicals chosen did not pose any danger with the experimental methods used.

d) Investigation of students’ understanding: In order to evaluate students understanding of the experiment, a variety of conceptual questions were developed for students’ to explore the functional group properties, examine experimental choices (design-based inquiry), derive a conclusion, and extend the utilization of data to other situations. The post-lab questions progressed from using lower cognitive thinking skills (such as recall and retrieval) towards questions that required knowledge utilization and analysis to make judgments about the molecules given and the tests needed (Post-lab Questions 1-3). Students were limited to performing only two tests in the laboratory as a pedagogical measure in prompting them to use their data to decide on further testing. This procedure prevented students from randomly testing their unknown which would result in a trial

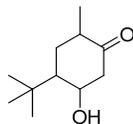
and error approach. Students must carefully review their observations to choose the two tests that would confirm their aroma category as they were penalized for additional tests.

Post-lab Questions:

1. Give your rationale for your choice in confirmatory test.
2. Given the following structures, what would you expect the compounds to smell like? Determine what chemical tests may be performed to confirm the functional groups present.



3. What chemical tests may be used to identify the functional groups in the following compound? What results would you expect from each test?



Implementation Results and Conclusions

This qualitative organic analysis experiment entitled “Identification of Functional Groups” (23) was performed by four introductory organic chemistry laboratory sections (65 CH 220L students), with students working collaboratively in groups of 2 or 3. Students observed and classified 18 compounds into nine groups (two from each functional group); however students were not told the expected number of groups or given any information about the compounds. Students came up with a wide range of descriptions for these chemicals and used very interesting adjectives in their characterization (Table 3.2). Instructions on the dangers of prolonged exposure to any chemical and the penalties for opening dropper bottles (as an incentive not to open or leave bottles open) were given prior to the start of the experiment. Students were able to group compounds by the characteristic aromas into 7-9 groups and presented their results to the instructor. If it appeared that students randomly grouped the chemicals, they were prompted to re-check aroma classifications based on their own descriptions.

Table 3.2. Some odor characterizations made by students.

Compound	Sample of Student's Characterizations
Formaldehyde	Almond, sesame oil, Fritos chips, latex paint, after effect nostril burning.
Acetic Acid	Vinegar, glue, rotten feet, nursing home, urinal tablet, cement.
Butylamine	Bleachy chlorine, ammonia, horse urine, hair perm, rotten fish, tuna.
Butanethiol	Bad garlic, rotten/burnt pumpkin seeds, sweetener, burnt pumpkin seeds.
Hexene	Cheap fruity perfume, gasoline, nail salon, paint thinner, rotten veggies.
<i>n</i> -Propyl acetate	Permanent marker, glue, nail polish remover, onion, mineral spirits.
Ethanol	Disposable lab gloves, hair product (dye), gin, vodka, pinesol/chlorox.
<i>N</i> -methylacetamide	Dirty diaper, stinky boy's locker room, nursing home, rotten flower.
Acetone	Moldy moth-balls, acetone, permanent marker, cheap vodka, rubber cement.

There were identifiable problems observed during the implementation of the experiment (Table 3.3). It is crucial that students use distinct, descriptive terms as they use these descriptions to group their compounds. For instance, classifying the aroma by pleasantness with general terms such as good, sweet, or bad was not helpful in classifying the aromas. The use of vague descriptions was a major contributor in the first three problems included in Table 3.3 where compounds were left ungrouped, additional categories were formed and compounds were placed in more than one group. This single deficiency contributed predominantly to the lower percentages of correct groupings of aldehydes, ketones and carboxylic acids. In these situations, students were not directly told their data was unacceptable, but were prompted to re-evaluate their observations (design-based inquiry experiment). The experiment promoted the importance of accurate observations and recording skills.

Table 3.3. Number and percentage of students with problems with olfactory observation or students who did not follow the directions.

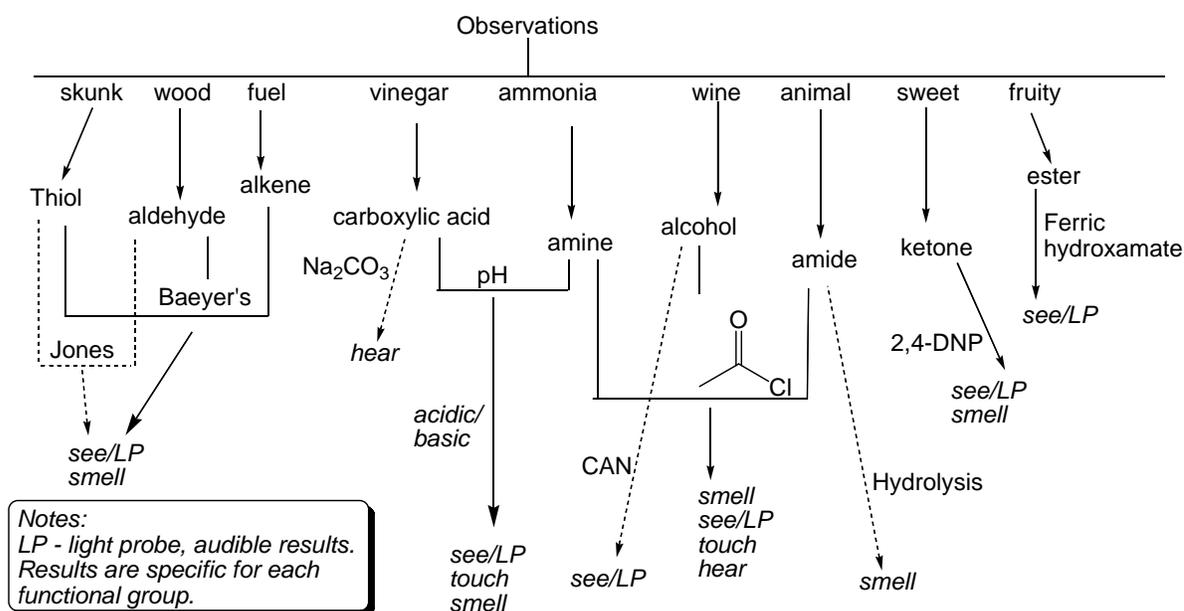
Identified Problem	Number of students	Percentage of the class
Not all compounds were grouped	6	9%
Characterized by pleasantness (not aroma)	5	8%
Overlapping compounds between groups	2	3%
<i>Unable to observe 1 -2 aromas</i>	<i>13</i>	<i>20%</i>

In future implementations of this experiment, students may be asked to show their initial results and provide *all* changes and/or revisions made to their data to illustrate their thought

processes. The inability to distinguish or detect one or two of the aromas was observed in 20% of the students. The majority of these students experienced this specifically with methanol, ethanamide and the carbonyl groups (except esters). In most cases only one compound in a group appeared to be difficult for students rather than both compounds. Substitutions for compounds that present the most difficulty for students to observe, could allow students to be better able to make classifications and aid students who had problems with one or two aromas to make better classifications. Potential replacements for methanol could include propanol or butanol and ethanamide with butyramide. In future implementations, students should be guided as to what constitutes useful descriptive terminology. Students may be referred to looking through flavor or aroma catalogs to guide their creativity. Since students do not know ahead of time the functional groups they are observing, this review should not influence their decisions about the aroma classifications, but rather enhance their ability to choose suitable characterizations. Students often need to be encouraged to discuss their individual assessments as a collaborative effort which allows students who are unable to observe specific aromas to be able to assign a characterization and correctly group the known compounds.

Although students had varying descriptions for each functional group, there were trends seen among genders. We found that a greater percentage of male students than females had difficulty in detecting certain smells. Eleven out of 40 males (28%) reported that methanol had no smell, while females appeared to have no difficulty discerning this odor. Two out of 25 females (8%) could not smell the ethanamide, while 10 out of 40 males (25%) did not detect any odor from ethanamide. In general, males had difficulty distinguishing and characterizing particularly sweet or pleasant odors, which is also reflected in the literature as differences in aroma perception among gender (24). Due to the differences shown by males and females, it is recommended groups be composed of both males and females.

After one or more rounds of deciding on classifications for the 18 known compounds, 72% of students correctly classified their unknown compound by aroma as reported in their post-lab (Scheme 3.2). Some students identified the functional group without stating the evidence for their determinations (14%). Others had inaccurate results that led to either misidentified unknowns therefore needing additional confirmatory tests to be performed (6%) or indecision between two groups before carrying out the chemical tests (6%). Table 3.4 includes examples of students' observations.



Scheme 3.2. Sensorial observations of functional groups with characteristic tests.

Table 3.4. Students' results for three confirmatory tests.

Unknown #	Test	Results
1 (Alcohol)	Acetyl chloride	<i>Smell:</i> "rubbing alcohol change to fruit like" "fruity banana" <i>See:</i> "smoky release" "turned brownish-red" <i>Touch:</i> "warmed up" "felt hot - exothermic rxn" <i>Hear:</i> "popping sound"
5 (Thiol)	Oxidation 1. Jones reagents 2. Baeyer's reagent	<i>Smell:</i> "smells like play-doh [from skunk-like]"; "sweet but unappealing smell" <i>See:</i> "Δ color: blue and green (dark) precipitate"; "Δ color: murky pond water, floating brown precipitate in milky-clear fluid" [from clear solution] <i>Touch:</i> "heat" <i>Hear:</i> "light probe – slightly slower than H ₂ O"; "decreased frequency w/ light probe"
6 (Carboxylic acid)	pH-acidic 1. Indicator 2. NaOH 3. Na ₂ CO ₃	<i>Smell:</i> "NaOH added made smell go away" <i>See:</i> "indicator turned to red/pink" <i>Touch:</i> "became warm" <i>Hear:</i> "light probe frequency was higher than indicator"; "there was fizzing"[Na ₂ CO ₃]

Students who used the light probe were able to connect an auditory response to the visual changes observed, even though some students had difficulty describing these observations in a scientific/technical manner.

- "The light probe was used to determine color intensities. When water was tested a rapid chatter (like a bat) was noted. When [With] our yellowish orange compound (precipitate of the 2,4-DNP test) we got a cyclic chipping."
- "Light probe: intensity decreases [with brown precipitate from Baeyer's reagent] compared to H₂O." or "the intensity of the frequency in the unknown tube [with precipitate of the 2,4-DNP test] was less than that in the clear [water] tube."

Using a rubric (provided in Appendix B) and coding by correctness, students' responses to the Post-lab Questions 1-3 were quantified. The average post-lab grade was 80±4%. A plot of the z-scores of the students' grades against density probability for each laboratory section showed a relatively normal distribution of the raw scores (Graph 3.1, with lines representing a visual guide) for three sections. Section 203 did not present the typical normal distribution when compared to the

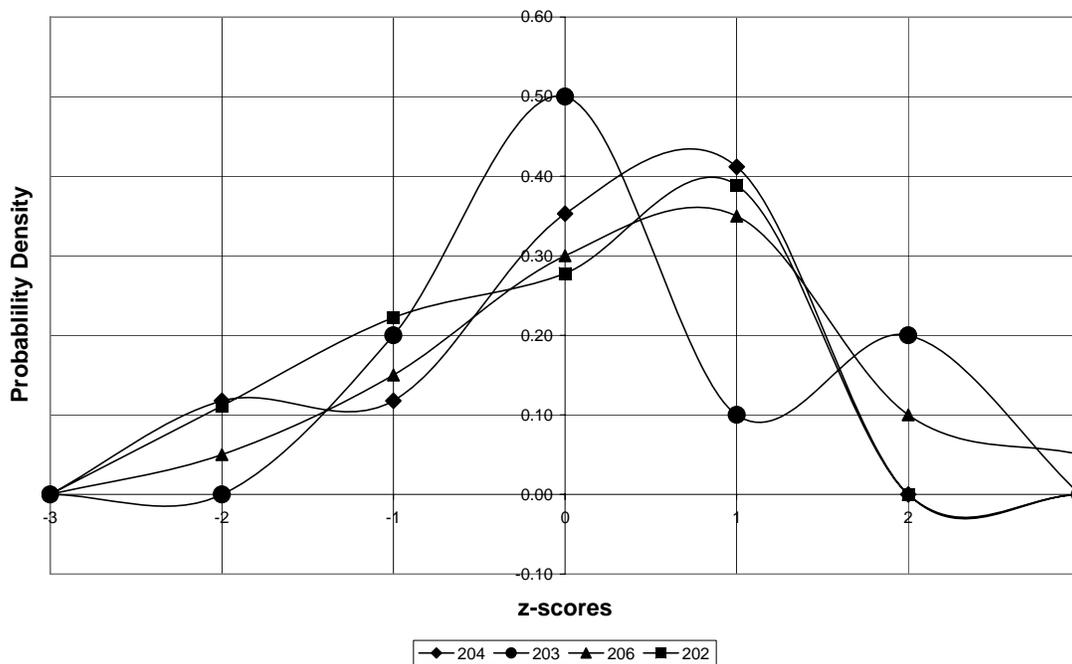
other sections. These z-scores are a measure of the standard deviation from the mean and used to make comparison between the different normalized data.

$$z = \frac{x - \mu}{\sigma}$$

, where x is the raw score, μ is the mean and σ is the standard deviation.

Section 203 was our pilot study and as a result of the observations with this section, minor changes to the procedure and questions were made. For instance, students in this section were not specifically asked to prepare a general procedure or conclusion (although few students did). The modifications may have contributed to the change from a binomial distribution to an even comparable distribution of scores.

Probability Density Data for Grades



Graph 3.1 Distribution of students' grades as the probability of z-scores (Normative data).

In addition to the quantitative results, students' feedback stated that they enjoyed the experiment and were surprised at the usefulness of the sense of smell. Some students' comments were:

-“This lab really surprised me on how accurate using your senses could actually be. I think this was a great lab (even though some of the material offended the senses)...”

-“I felt this was a very fun lab. Very interesting and felt that I could relate it to my everyday life. I felt this was the best lab of the semester.”

-“I thought this was an informative lab experiment to show how important our sense of smell can help in everyday chemistry.”

3.3 Esterification Kinetics Experiments

Esters are formed from the condensation reaction of a carboxylic acid and an alcohol and may be catalyzed using an inorganic acid under heat conditions (22). In order to control the position of the equilibrium of the Fisher esterification reaction and study the kinetics, various factors were altered to observe the effect on the reaction. The kinetics in relation to the structure can also be explored by changing the alcohols (22, 25) and/or the carboxylic acids (26) and comparing the rates of the reaction of various chain lengths and branches. Traditionally, esterification kinetics studies are performed spectroscopically such as by GC (27), GC-MS (28) and NMR (29), in which the ester formed or starting materials consumed may be monitored during the progress of the reaction while a variety of factors are varied. Most esterification studies, however, explore the synthesis of the esters where students determine the percent yield of their products and/or observe the aromas of the esters. Puterbaugh et al. developed an experiment for beginning organic chemistry students to use a modified Dean Stark trap (made from inexpensive materials) for azeotropic removal of water from

the esterification reaction where students determined the yield and identified the ester by IR (30). Birney and Starnes developed a combinatorial Fischer esterification experiment which includes simultaneous synthesis of numerous compounds and uses smell as a selective assay to identify methyl salicylate (the characteristic odor of wintergreen) (31). Williamson and Little presented a microscale experiment in which students synthesize a variety of esters, observe the aromas and note the solubility in water (32). Several other similar Fischer esterification experiments exist from a variety of sources such as chemical education literature (33), experimental procedures from instructor's websites (34) and laboratory manuals (35).

Typical undergraduate kinetics experiments (other than esterification reactions) utilize spectroscopic methods, potentiometric determinations or color changes to monitor the rate of the reaction. Holmes utilized the color change from the reactions of permanganate with Fe^{2+} and $\text{C}_2\text{O}_4^{2-}$ for students to observe the nature of the reactants, the concentration of the reactants, the presence of the catalyst, and temperature of the reaction mixture (36). Pfennig presented a chemical demonstration of an oxidation–reduction iodate, sulfite and thiosulfate clock reaction involving red and green colors monitored using a pH meter (37). Cooper and Koubek have used peroxide and iodide to demonstrate the effect of a catalyst (MoO_4^{2-}) on the rate of a chemical reaction (38). Schreck has developed a kinetics experiment to determine the rate constant for the reaction of methyl iodide and potassium *tert*-butoxide, determining the concentration by taking aliquots of the reaction at appropriate intervals and titrating with perchloric acid using phenolphthalein as an indicator (39).

Since many esters have naturally occurring aromas that are pleasant and easily recognized (30), this sensorial experiment allowed students to identify the esters by smell rather than instrumentation and to determine the rate of esterification by the emergence of the ester aromas. The typical ester yield from Fischer esterification experiments is approximately 60-70% for equal amounts of the reactants and higher when one of the reactants is increased (34). This permits the observation

of aromas easily and manipulates the kinetic experiment to observe factors affecting the rate of esterification. In order to develop this experiment, a variety of considerations were explored:

- i) Selection of easily recognizable esters.
- ii) Consideration of factors that affect rate of reaction.
- iii) Determination of appropriate chemical testing.
- iv) Consideration of safety concerns regarding the use of smell.
- v) Investigation of students' understanding of the experiment.

i) Selection of esters: The esters were chosen based on aroma familiarity by students (to be recognizable) and comparable odor thresholds of resulting esters. The esters that were chosen allowed students to characterize the compounds distinctly as the aromas resemble those from fruits, perfumes, cleaning supplies, etc. The first part of the experiment requires students to creatively characterize the aromas of the ester produced. The MSDS data and related literature (20) for the esters chosen were reviewed for the reported characteristic aromas (pure). These compounds were then synthesized in the laboratory to characterize the *observed aromas* (Table 3.5). Some aroma characterizations of the larger esters such as the *tert*-butyl esters were not reported. The pivalate (trimethyl acetate) esters exhibit a mix of fruity or sweet and medicinal aromas therefore were excluded from the esterification kinetics studies. Although, some of the *t*-butyl esters also produce a medicinal odor, these possessed a predominately fruity aroma and so they were considered for further examination.

Table 3.5. Reported aroma descriptions and observed aromas from ester synthesized in the research laboratory prior to use in the kinetics studies.

(No reported aromas indicated with * and aromas observed in the lab in *italics*).

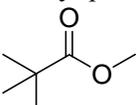
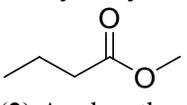
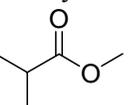
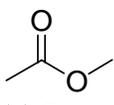
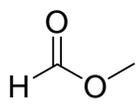
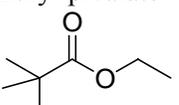
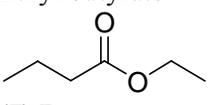
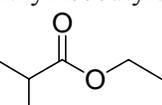
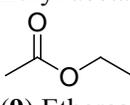
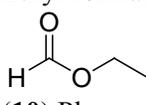
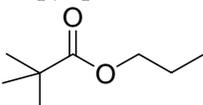
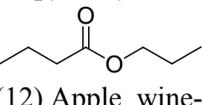
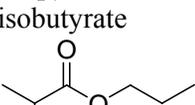
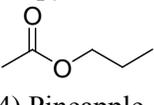
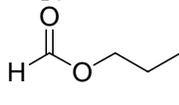
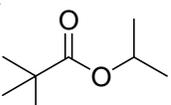
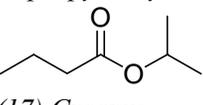
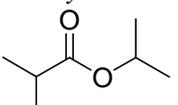
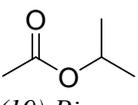
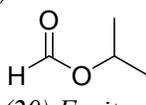
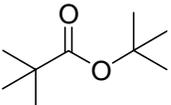
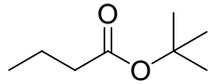
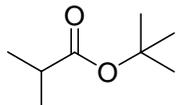
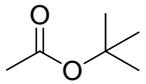
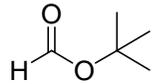
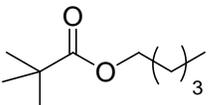
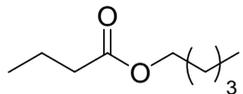
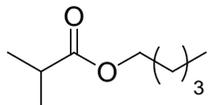
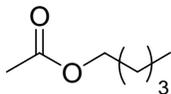
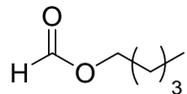
<p>Methyl pivalate</p>  <p>(1) Acetic, <i>fruity antibiotic medicine</i></p>	<p>Methyl butyrate</p>  <p>(2) Apple, ethereal, pineapple, <i>strongly fruity, bubble gum like</i></p>	<p>Methyl isobutyrate</p>  <p>(3) Fruity, floral <i>pineapple</i></p>	<p>Methyl acetate</p>  <p>(4) Sweet, ethereal, <i>faintly sweet</i></p>	<p>Methyl formate</p>  <p>(5) Ethereal, <i>faintly sweet</i></p>
<p>Ethyl pivalate</p>  <p>(6) Camphor, blueberry, <i>sweet, medicinal</i></p>	<p>Ethyl butyrate</p>  <p>(7) Banana, pineapple, sweet, <i>pineapple, rum-like</i></p>	<p>Ethyl isobutyrate</p>  <p>(8) Citrus, strawberry, <i>fruity alcoholic, strawberry</i></p>	<p>Ethyl acetate</p>  <p>(9) Ethereal, <i>fruity, pineapple, sweet nail polish</i></p>	<p>Ethyl formate</p>  <p>(10) Pleasant, <i>fruity wine-like odor, bubble gum</i></p>
<p>Propyl pivalate</p>  <p>(11)* sweet, medicinal</p>	<p>Propyl butyrate</p>  <p>(12) Apple, wine-like, honey, apricot pineapple, <i>fruity candy</i></p>	<p>Propyl isobutyrate</p>  <p>(13) Ripe <i>fruity, tropical, melon berry, pineapple, sweet fruity</i></p>	<p>Propyl acetate</p>  <p>(14) Pineapple, rum, celery, pear, <i>fruity, berry</i></p>	<p>Propyl formate</p>  <p>(15) Berry, green, rum, ethereal, <i>sweet</i></p>
<p>Isopropyl pivalate</p>  <p>(16)* <i>fruity medicine</i></p>	<p>Isopropyl butyrate</p>  <p>(17) Creamy, pineapple, sweet, green, <i>fruity alcoholic drink</i></p>	<p>Isopropyl isobutyrate</p>  <p>(18) Refreshing pineapple, citrus, pear, pear, <i>orange-strawberry</i></p>	<p>Isopropyl acetate</p>  <p>(19) Pineapple, <i>fruity, sweet, fruity bubble gum</i></p>	<p>Isopropyl formate</p>  <p>(20) Fruity, pleasant, cocoa, tropical, <i>Strongly fruity</i></p>

Table 3.5. Reported descriptions and observed aromas (continued).

<p><i>tert</i>-Butyl pivalate</p>  <p>(21) Fruit odor, Medicinal (not very fruity)</p>	<p><i>tert</i>-Butyl butyrate</p>  <p>(22)* Medicinal banana</p>	<p><i>tert</i>-Butyl isobutyrate</p>  <p>(23)* Strong fruity, slightly medicinal</p>	<p><i>tert</i>-Butyl acetate</p>  <p>(24)* Faintly fruity</p>	<p><i>tert</i>-Butyl formate</p>  <p>(25)* Sweet minty</p>
<p>Amyl pivalate</p>  <p>(26)* candy, pineapple like</p>	<p>Amyl butyrate</p>  <p>(27) Banana, cherry, pineapple, tropical, fruity candy</p>	<p>Amyl isobutyrate</p>  <p>(28) Apple, banana, apricot, Apple, apricot</p>	<p>Amyl acetate</p>  <p>(29) Banana, earthy, ether, strong fruity banana-apple like, pear</p>	<p>Amyl formate</p>  <p>(30) Fruity, earthy ethereal, unripe banana, orange-apple mix, earthy</p>

Reported threshold values, volatility and hazards (40) were used in selecting the esters that possessed similar properties to prevent confounding factors affecting the time for the emergence of the ester aroma. The esters chosen had moderately high volatilities and low odor threshold values which would allow students to observe them easily at a relatively low concentration. Small molecule esters (low molecular weight) with similar volatility and odor threshold values were the best candidates (Table 3.6) (40). Based on this information, methyl and methanoate esters were discarded as candidates from the final experiment.

Table 3.6. Representative values for odor thresholds and volatilities for selected esters.

Compound	Odor threshold, ppm	Volatility, mmHg	Molecular weight, g/mol
Methyl butanoate (2)	60-76	40 at 30°C	102.13
Methyl isobutyrate (3)	7	36 at 20°C	102.13
Methyl methanoate (5)	130	476 at 20°C	60.05
Ethyl butanoate (7)	1.0	16 at 20°C	116.16
Ethyl ethanoate (9)	0.9	73 at 20°C	88.12
Ethyl methanoate (10)	31	194-201 at 20°C	74.08
Propyl ethanoate (14)	0.6	43 at 20°C	102.13
Propyl methanoate (15)	1.0	59 at 25°C	88.11
Pentyl ethanoate (29)	0.1	27 at 20°C	130.19

The Fisher esterification reactions of each ester performed under the same conditions gave a reasonable comparison of the aroma properties of the esters. The theoretical yield and odor thresholds also provide a basis to determine the success of the experimentation. The theoretical yield of the Fisher esterification is ~85-90% when the moles of one reagent are double the moles of the other reagent (40,41). The resulting concentration of the synthesized esters was estimated to be higher than the odor threshold values (concentration necessary to observe) under the assumptions of 100% yield (sample calculations shown in Figure 3.2). Therefore, the concentration of the esters necessary to observe the aromas would exceed the literature values making them relatively easy to perceive.

Approximate volume of air around esterification apparatus				
Width (hot plate) = 12 cm				
Height (from flask to fan) = 9 cm				
Depth (from observer to flask) = 30 cm				
Volume = width x height x depth			Volume	Volume
			3240 cm ³	3.24 L
Reagent added	Measured equivalent volume	Moles		
7 drops ethanol	<0.1mL	<1.7mmol		
28 drops 0.2M acetic acid	2.0mL	0.4mmol		
Ester and MW	moles	Mass	Density	Volume
propyl acetate (14), 102.13 g/mol	0.0004 mol	0.0408 g	0.880 g/mL	0.046 mL
ethyl acetate (9), 88 g/mol	0.0004 mol	0.0352 g	0.897 g/mL	0.039 mL
Esters	Concentration ester in air	Concentration	Odor threshold	
propyl acetate	1.42×10^{-5} L/L	14.2 ppm	0.6 ppm	
ethyl acetate	1.21×10^{-5} L/L	12.1 ppm	0.9 ppm	
<i>Assumptions:</i>				
1. At 100% efficiency of esterification reaction				
2. All of synthesized ester evaporate				
3. Volume of air observed occurs primarily within a specific area in front of the fan				

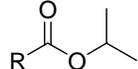
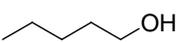
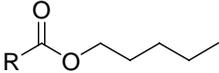
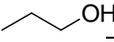
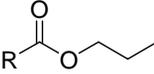
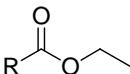
Figure 3.2. Sample calculations to approximate concentration of esters in air for the ethyl and propyl acetate (ppm).

ii) Factors affecting esterification: Various factors that affect the rate of esterification were explored in terms of the time taken for a critical concentration of the ester to form and then be detected by smell. Typical factors that are explored in rates of reaction experiments are concentration, pressure, temperature, catalyst, solvent and nature of the reactants (chemical or physical properties) such as size shape, sterics and physical state. The effect of each factor on the reaction, the time needed to complete the experiment and the ability of the students to fully utilize these factors were evaluated to decide which factors suitable to explore in the freshmen teaching laboratory. The effects of sterics, varying the concentration of carboxylic acid, amount of the alcohol, and acid catalyst were chosen for this study. The observation of each of these factors by different groups, in which students then share data, provides enough time to complete the lab within

2.5 hours including time for their post-lab questions. Heating and cooling needed for the observation of temperature effects poses a challenge due to time constraints of the laboratory as it takes time to reach and maintain 65°C. Deionized water was used as the solvent because it was odor free and does not interfere with the ability for students to observe the aromas distinctly. In order to observe the aromas, the reaction system must be open which prevented the observation of pressure effects on the reaction to be explored.

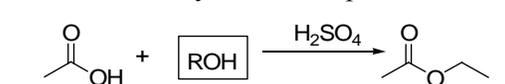
iii) Testing: The esterification reactions were performed with the most suitable ester candidates (explained previously) to explore the data obtained by this method, determine if the data would consistently give accurate results and determine which of the ester candidates were the most viable to be synthesized in the undergraduate lab. The kinetics in relation to the molecular structure was studied by changing the types of alcohols and/or the carboxylic acids and comparing the rates of the reaction of molecules containing various chain lengths and branching (Table 3.7).

Table 3.7. Average results obtained when assessing the rate of esterification reactions performed in the research laboratory.

Reaction	R from carboxylic acid =	Average Time				
		H	Me	Pr	Is-pr	t-bu
		68 sec $n=6, \pm 2$	79 sec $n=6, \pm 2$	75 sec $n=6, \pm 2$	136 sec $n=6, \pm 2$	285sec $n=2, \pm 3$
		42 sec $n=3, \pm 2$	50sec $n=3, \pm 2$	84 sec $n=3, \pm 2$	105 sec $n=3, \pm 2$	221sec $n=2, \pm 3$
		35 sec $n=6, \pm 2$	51 sec $n=6, \pm 2$	56sec $n=6, \pm 1$	107 sec $n=6, \pm 2$	189sec $n=3, \pm 2$
		30 sec $n=6, \pm 2$	33 sec $n=6, \pm 2$	35sec $n=6, \pm 2$	45 sec $n=6, \pm 2$	80sec $n=2, \pm 4$
MeOH		5 sec $n=6, \pm 2$	21 sec $n=6, \pm 2$	26sec $n=6, \pm 2$	29 sec $n=6, \pm 2$	56sec $n=2, \pm 3$

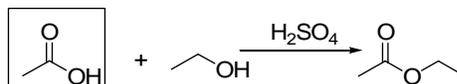
The evaluation of the data was relatively consistent with the experimental hypothesis and showed generally that structural effects can be observed using this method. The concentration of carboxylic acid, amount of the alcohol used and acid catalyst produced reasonable data in the research laboratory demonstrating its reliability and suitability to demonstrate these factors (Table 3.8). The *tert*-butyl esters form slowly due to the significant steric bulk in the tetrahedral intermediate creating an energetically unfavorable situation and therefore these esters were excluded from the kinetics experiment.

Table 3.8. Average results when evaluating the factors affecting the rate of esterification in the research laboratory. Each data point had a deviation of ± 2 seconds and $n=6$ trials.



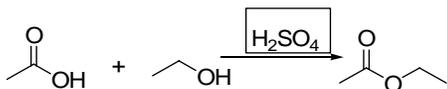
Drops of Alcohol	Average Time, sec
1	105
2	83
5	48
7	31
10	26

Vary Amount of Ethanol



Concentration, M	Average Time, sec
0.1	40
0.2	30
0.5	21
1.0	11
2.0	7

Vary Concentration of Acetic Acid



Amount of H ₂ SO ₄	Average Time, sec
1 drop	66
2 drops	46
5 drops	30
10 drops	23
20 drops	21

Vary amount of catalyst

Standard Conditions

5 drops conc. H₂SO₄
7 drops of Ethanol
28 drops 0.2 M Acetic Acid

iv) *Safety*: The observation of esters in this kinetics experiment presents some unique challenges in addition to those experienced from the typical esterification synthesis and kinetics

experiments (described previously). The MSDS data and relevant literature (20,40) for all esters was examined to determine the potential hazards. The carboxylic acids used to make these esters were diluted to 0.2M preventing them from producing an overwhelming aroma. The observation of the aromas must be done reliably from a safe but consistent distance (changes in distance may affect time). The esterification experimental set-up provided a reasonable distance from the observer to prevent harm from the heating source and over-exposure to chemicals, but close enough to allow the observation of the aromas in a timely fashion. This was made possible by the use of a hand-held battery powered fan to circulate the ester aroma. The set-up was placed 30 cm (~12 inches) between the observer and the reaction flask (Figure 3.3). These fans were purchased inexpensively (~\$1 per fan). Coffee crystals were also available to students between trials to “cleanse” their olfactory senses.

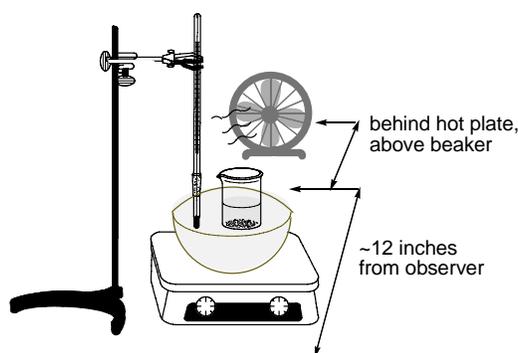


Figure 3.3. Esterification experimental set-up.

v) *Investigate students' understanding:* A variety of conceptual questions were developed to guide students understanding of the esterification kinetics experiment, the factors affecting the esterification, derive a conclusion and apply the concepts learned to other situations. The questions developed allow students to construct answers from their data rather than just recalling experimental details allowing students' metacognition thinking, knowledge utilization and analysis skills to be examined. Students used their data with aid of the questions to make generalizations (comprehension) and used their data to solve problems on the factors affecting the rate of the

esterification reaction (analysis and knowledge utilization skills). Based on students' responses, it was observed that students applied concepts to new situations (knowledge utilization) and determined sources of error (metacognitive thinking).

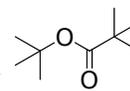
Similar to the organic analysis experiment (Section 3.1), the report for this experiment consisted of pre-lab questions, reporting results with tables, as well as answering short conceptual questions. The pre-lab questions required students to review information on functional groups, mechanism of the Fisher esterification and factors that would affect the rate of a reaction, which they may be able to derive from the experiment but also obtain from any general chemistry text. The post lab questions explored students' understanding of the factors affecting the experiment, speculate the rate of formation for a given molecule and deduce other factors that affect the reaction.

Students were asked to explain the factors affecting their observation times with respect to structural effects, changes in concentration and the amount of the catalyst. The relative rate of formation for *tert*-butyl pivalate was explored with relation to the data observed (Post-lab Questions 1-4). Students were asked to determine how temperature affected the rate of a reaction and potential sources of error of their experiment. A rubric (provided in Appendix C) was established to characterize students' responses by the degree of correctness and completeness for each question in order to summarize their results into categories (see Results and Conclusions). This method was used to infer the effectiveness of the questions in gauging students understanding of the concepts and implications of the data.

Post-lab Questions:

1. With respect to Table 5 (effect of catalyst), what conclusions can be drawn about the rate of reaction with respect to the sulfuric acid catalyst? Comment on how the catalysts affect the energetics of the reaction.

2. Based on your observations, what would you expect the rate of formation of to be? Explain.



3. Predict what would happen to the rate of the reaction at various temperatures (high to low), knowing that this reaction is endothermic.

4. What are the potential sources of error associated with this experiment?

Implementation Results and Conclusions

This Fisher esterification synthesis experiment studied the esterification rate of reaction by exploring the amount of time taken for a critical concentration to be detected by the sense of smell using the time of emergence of the ester aroma formed during the reaction (42). Eighty-nine introductory organic students in four laboratory sections performed this experiment. The experiment was written as a guided inquiry laboratory in which students explored the topic with minimal instruction and were asked to draw conclusions about the nature of the esterification reaction. Students prepared a brief procedure, answers to the pre-lab questions, reported their results, and conclusions, and answered post-lab questions in an average of two hours and thirty minutes. The criteria for the rubric used to characterize students' responses included correctness and completeness of their answers. The percentages of students who correctly and completely answered pre-lab questions (C &C), students who provided correct but not complete responses (C) and students who either did not answer the question correctly or completely (N) are shown in Table 3.9.

Table 3.9. Percentages of student responses characterized by correctness and completeness (C&C), correct but not complete (C) or did not answer the question correctly or completely (N).

Pre-lab Questions	C&C	C	N
1. Review the functional groups used in this experiment (carboxylic acids, alcohols and esters) with respective nomenclature, structure and properties.	80%	0%	20%
2. Write a generic mechanism for an acid-catalyzed Fisher esterification.	72%	3%	24%
3. Find at least 2 factors that can affect the rate of a reaction.	59%	6%	34%

Seventy-two percent of students provided a fairly complete and correct generic mechanism for the esterification reaction which included the intermediates, the correct use of arrows and the correct steps (Figure 3.4), while 24% of students only gave the generic equilibrium reaction as the mechanism (Table 3.9). Three percent of students drew a complete mechanism for the esterification reaction but multiple arrows or steps were missing. Seven percent of students provided an explanation of each step in their mechanism (Figure 3.5) and one student did not draw a mechanism, but provided a narration of the mechanism steps. Eighty percent of students presented complete information on esters, alcohols and carboxylic acids in a table, which they used in deciding on the reagents needed. While most students provided generic factors that affect kinetics reactions, 9% of students gave responses based on the experimental procedure (C&C response - two factors and C response - one factor). Two students gave factors affecting the reaction specifically addressing the effect on the equilibrium.

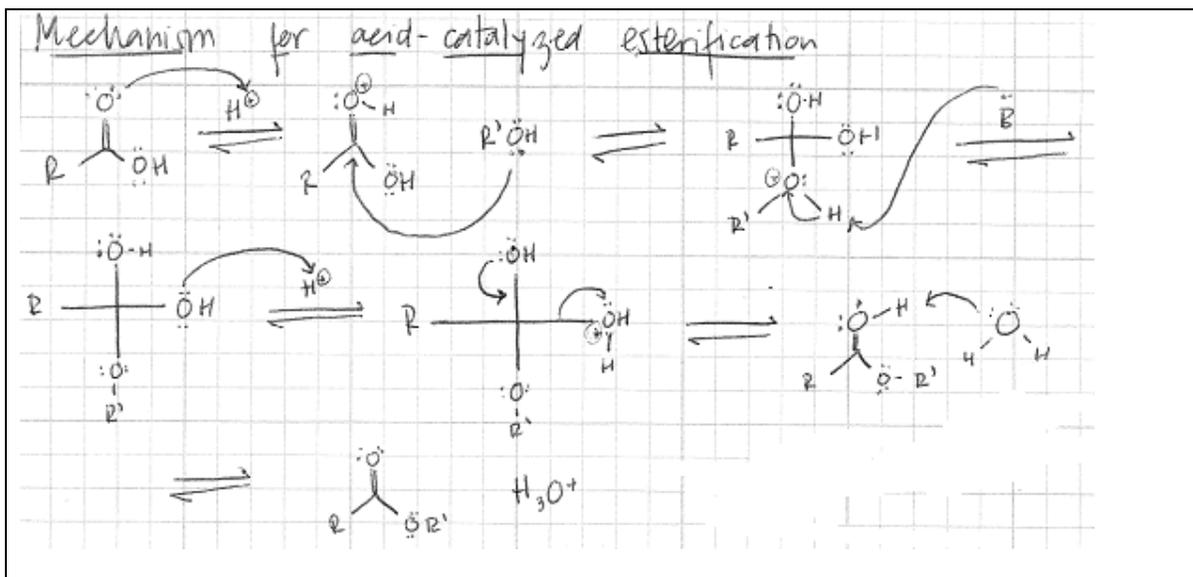


Figure 3.4. Students' esterification mechanisms.

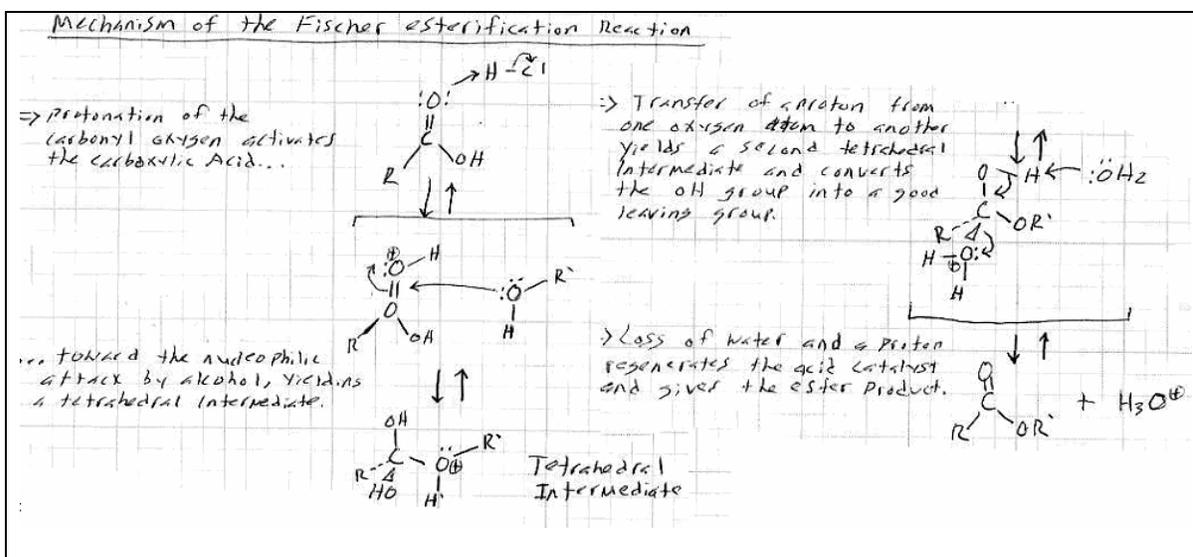
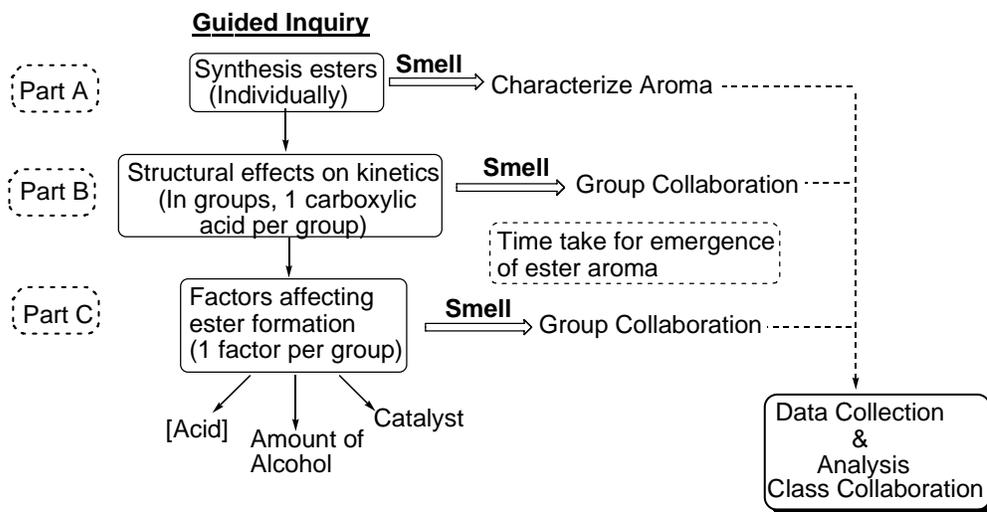


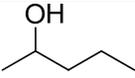
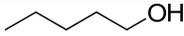
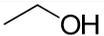
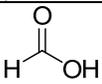
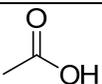
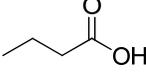
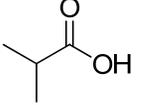
Figure 3.5. Esterification mechanism with explanations for each step.

During the first part of the experiment (Part A, Scheme 3.3), each student synthesized an ester (individual work) and categorized this synthesized ester by aroma. Students used a wide range of descriptions (Table 3.10) and collected all the other classifications from the lab participants.



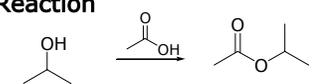
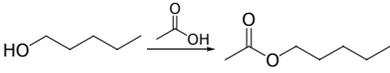
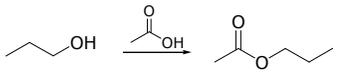
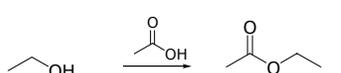
Scheme 3.3. Flow chart of the esterification kinetics experimental procedure.

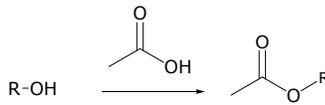
Table 3.10. Students' descriptions of observed aromas for Part A.

					Me-OH	← Alcohols ↓ Acids
Rubber	Flowers, apricot	Peaches, glue, new shoes, soap	Fruity glue, lemon, marker, runts candy	Fruit, lemon, crisp linen, moonshine, sweet, melon	Ether like, rubber, flowers, fabric softener	
Alcohol, marker, paint thinner	Cucumber, grapes, rubber cement	Pears, hair spray, fruit	rum, pears, glue	Elmer's glue, liqueur, apple	Fruit smell, marker, citrus	
Banana alcohol, pineapple	Sour apple	Cheese, markers	old fruit, marker, apple	Cherry, strawberry, apple, banana, grapes	Paint, bubble gum	
Citrus, feet, rubbing alcohol	Apple, feet	Apples, rum, hair spray	banana, banana chips, strawberry, pineapple	Apples, pineapple, grape	Pears, bubble gum, strawberry	

In *Part B*, students explored structure-activity relationships and observed general trends from the effects of chain lengths and steric bulk on the emergence of the ester aroma (Table 3.11). In groups of 2-3 students, they were assigned a carboxylic acid in which they performed kinetics studies with 4 alcohols. Students monitored the time it takes for emergence of the ester aroma from the reaction of their assigned carboxylic acid with each alcohol (with at least 2 trials), recording the data in seconds. The students collected the data of the other carboxylic acids from all groups in order to complete a table and analyze each reagent's effect (Scheme 3.3).

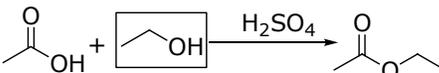
Table 3.11. Sample data from students on effects of alcohols for Part B.

Reaction		Average Time for Emergence of Aroma
		18±3 sec n=2
		29±5 sec n=3
		22±3 sec n=3
		17±3 sec n=2
Data for 1 lab section of 10 groups, n=groups		

R-OH	Acetic Acid	Product
		
Group 1		
R= Et	Pr	Is-pr
30sec	37sec	51sec
Group 2		
R= Et	Pr	Is-pr
12sec	39sec	40sec
Student variability with increasing trend.		

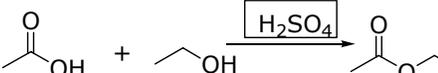
The final portion of the experiment (*Part C*) involved monitoring the emergence of the ethyl acetate aroma while varying the acetic acid concentration, amount of the alcohol, or the amount of the catalyst (concentrated sulfuric acid). Each group is assigned one factor to vary and the remainder of the data is collected from the other groups. The students gather data to draw conclusions on the structure-activity relationships and factors affecting the reaction via leading questions in the post lab related to *Parts B* and *C* (Table 3.12). Students were not explicitly told about expected trends but given general instructions, prompted as to the time constraints, asked to study the results of the esterification reaction and provide conclusions.

Table 3.12. Sample data for ethyl acetate aroma detection by varying the amount of (a) ethanol, (b) catalyst and concentration of acetic acid (c).



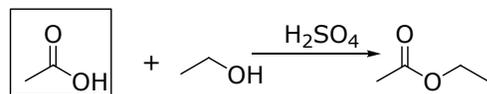
Drops of Alcohol	Time, sec
1	56 ±2
2	46 ±2
5	39 ±2
7	35 ±1
10	32 ±1

a



Drops of H ₂ SO ₄	Time, sec
1	61 ±2
2	35 ±2
5	25 ±3
10	18 ±2
20	16 ±2

b



Concentration, M	Time, sec
0.1	32 ±2
0.2	23 ±2
0.5	16 ±2
1.0	13 ±1
2.0	9 ±1

c

Standard Conditions
 5 drops conc. H₂SO₄
 7 drops of Ethanol
 28 drops 0.2 M Acetic Acid
 n=4 groups

The data varied slightly among the groups, however general trends were observed (Table 3.11). It was important that students maintain the 30 cm distance between the reaction and themselves as students who moved the experimental set-up experienced significant differences in their trials and needed to repeat their trials several times. To prevent this problem, it must be stressed that students maintain their kinetics set-up and a ruler or marker can be provided to mark the distance that must be maintained. Students who were unsuccessful in controlling their hot plate also experienced differences in their data.

This kinetics experiment utilized the sense of smell allowing students to explore the synthesis of various esters and study the kinetics of these Fischer esterifications without the use of

instrumentation or specialized equipment in an efficient and safe manner. Students used both individual and group data to rationalize the results and drew conclusions about the rate of the esterification reaction and the factors that affect it. The percentage of students who correctly and completely (C &C), correctly but not completely responses (C) and neither correctly or completely (N) answered each post lab question are shown in Table 3.13.

Table 3.13. Percentage of student post-lab responses characterized by correctness and completeness (C&C), correct by not complete (C) or did not answer the question correctly or completely (N).

Post lab Questions	Concepts	C&C	C	N
1. Table 2 - analysis	Structure-Activity	45%	43%	11%
2. Table 3 - analysis	Concentration of alcohol -factor	14%	77%	8%
3. Table 4 - analysis	Concentration of carboxylic acid -factor	29%	59%	11%
4. Table 5 - analysis	Catalyst	32%	55%	11%
5. knowledge utilization	Rate of <i>tert</i> -butyl pivalate	66%	21%	14%
6. analysis	Aroma trends	62%	17%	18%
7. knowledge utilization	Temperature effects	53%	24%	23%
8. metacognition	Recognition of experimental errors	62%	16%	20%

Students explored how factors of size, branching, quantities of reagents and catalyst affect the formation of ester, which are inferred by the development of the ester aroma from the reaction. Correct responses stated that increased quantities and small sized reagents with minimal branching affected the forward direction at a faster rate (questions 1-4). The C&C responses included a rationale for the effects on the reaction equilibrium (questions 1 -3). Specifically, these students deduced why the trends in the size and branching of the starting reagents affected the rates of detection of aromas and explained that the effect of the catalyst occurs up to a point (after 10 drops) and lowers the activation energy of the reaction (question 4) (Table 3.13). These rates of detection were used to infer effects on the rate of the reaction.

Students stated that the rate of formation of *tert*-butyl pivalate would be faster or slower than their data (C response) or applied their data to determine qualitatively that the rate was slower based on the steric bulk of the molecule (C&C). Two students suggested an approximate time they would

expect based on the data they obtained, while two other students stated the reaction would be slower due to carbocation stability even though their mechanism indicates no carbocation intermediate. A complete response to Pos-lab Question 7 included the effect of temperature changes on the rate of an endothermic reaction without an explanation. Some students suggested that higher temperatures may provide more energy needed for the endothermic equilibrium to generate more products, cause other side reactions or cause loss of products at very high temperatures (C&C). Three students determined potential competing reactions that could occur in the esterification reaction and in particular determined that these may occur as a result of the reversibility of the reaction or side reactions of the reagents (C&C).

Post-lab questions addressed chemical aspects of esterification kinetics. However, students added their opinions about this experiment and we considered these relevant to its success as a laboratory experience. Out of 15 students that gave informative non-solicited feedback about their experience in the lab, 8 students commented that the experiments aided them in learning various aspects about the reaction studied, 7 commented on real world applications such as aroma chemistry, 5 on the nose as an analytical tool, and 11 related to the experiment as a good learning experience. One of the students' comments summarizes the positive comments obtained: "I thought the experiment was good because being the measuring device was interesting. To know when it was happening without the fancy machines was nice. It also gave good insight into the different contributors to reaction speed, with noticeable changes which we measured."

Sixteen percent of students gave feedback on potential improvements such as performing less kinetics studies per group and the inclusion of established break times (although it was admitted that other groups may work slower impeding this process). Negative comments included more time needed for the experiments, stronger or weaker aromas or not obtaining results they expected to get. From the students' comments, future use of this experiment could incorporate more connection to

real world applications, the potential benefits of this olfactory kinetics method and more structured laboratory time (without losing the inquiry aspect of the experiment). To incorporate a more structured laboratory session, it may be possible to incorporate additional sensory observations through demonstrations or short activities with class collaboration in between each experimental section. Future implementation of this experiment could include the use of the LLR to make further inferences on this experiment's impact with comparison to a control group performing a traditional experiment (discussed further in Chapter 4). Additional student responses to each post-lab question and the esterification mechanism are available in Appendix C.

3.4 Equilibrium Experiments

Dynamic chemical equilibrium occurs when the forward and reverse reactions proceed at the same rate and under specific conditions as they may be affected by various situations. Typically, qualitative equilibrium experiments have been monitored by visual observations to demonstrate the Le Chatelier's principle (LCP) (43). Recent literature on qualitative equilibrium experiments have focused primarily on visual changes such as the reactions of lead solutions leading to the formation of yellow or white precipitation (44) and the observation of dynamic equilibrium using cobalt complexes with the color changes between pink and blue (45,46). The innovative approach by Anderson and Buckley used an interactive demonstration that explores equilibrium constants, K_{eq} , and acid-base properties using the sense of smell (Chapter 1) (47). Other researchers have explored the topic quantitatively using UV-Vis spectrometry to study the $\text{Co}(\text{H}_2\text{O})_6^{2+}/\text{CoCl}_4^{2-}$ equilibrium (46) and the spectrophotometric absorbance measurements of iron and thiocyanate solutions to explore K_{eq} (48).

Instead of new experimentation, some researchers have focused on the understanding of chemical equilibrium such as a study demonstrating students' difficulties with chemical equilibrium using a structured laboratory instruction (49). Tyson et al. reviewed the usefulness of the concepts such as LCP, equilibrium law and reaction rates to explain equilibrium changes in the formation of ammonia. They presented students' interpretation of terminology (such as the position of equilibrium and closed systems) which showed that students have difficulty with physical and chemical states (50). Some research has focused on investigating students' conceptual changes (learning that changes an existing idea) with chemical equilibrium (51) and cognitive apprenticeship which occurs when students observe, perform and apply concepts learned with help from an instructor (52). However, a multi-sensory approach to make determinations on the nature of equilibrium reactions and creatively explore the LCP has not been explored.

This multi-sensory equilibrium experiment was developed to study the LCP by observing visual (color, solution viscosity and presence of a precipitate), temperature, aroma, and sound changes in a variety of equilibrium reactions. The LLR was utilized with this multi-sensory experiment to provide students with a unique and structured inquiry experience. To incorporate these two new dimensions (the use of multiple senses to explore equilibrium reactions and the LLR) into this Le Chatelier experiment, chemical and pedagogical objectives were set and explored. The chemical objectives included:

- a) Selection of appropriate chemical equilibrium reactions that allow for multi-sensory observations.
- b) Chemical testing to screen for suitability and use with undergraduates.
- c) Safety and practical issues related to the multiple sensory determinations.

a) Selection of equilibrium reactions: A variety of equilibrium experiments were explored for their ability to incorporate two or more senses to make determinations on the concentration changes of the products and the reactants. The sources used came from literature (44-48), text-books

(53), online resources (54) and laboratory manuals (43). Six types of chemical equilibria were chosen to give students an overview of equilibrium reactions within a two-hour laboratory period. The chemical equilibria observed in this experiment were: acid-base, solubility (chemical and physical changes), common ion effect, complex ion and $\text{CrO}_4^{2-} \rightarrow \text{Cr}_2\text{O}_7^{2-}$. Equilibria were chosen based on the characteristics of *all* the reactants and products or replacement of reagents that would provide multiple sensory observations. Some reactions involved volatile organic compounds or ammonia which allowed for the observation of aromas recognizable to students. To incorporate sounds in some of the reactions, the typical base (where the specific base was not critical) was replaced with Na_2CO_3 to produce CO_2 (fizzes) in the presence of an acid. A light probe (lp) was also used to observe visual changes audibly, as the reactions chosen produced significant color or clarity changes (precipitation) that could be detected with the light probe. Several reactions had distinguishable enthalpy changes (ΔH), allowing temperature changes to be monitored.

In order to observe temperature changes, the ΔH of the equilibria were considered (Table 3.14) (55). The degree to which the temperature changes can be observed by touch was considered in the testing of the reactions and was concentration of the reagents. As a result of the effect of concentration, even reactions with high ΔH values may be observed as having no temperature change, as the concentrations used were too low to provide those observations. Due to safety concerns, it was necessary to use low concentrations of some reagents. Additionally, the enthalpy (ΔH) values may be provided or researched by students. Additionally, the sign of the enthalpy can be explored experimentally (physically determining negative or positive ΔH values), providing a learning opportunity for equilibrium concepts to be extended into thermochemistry concepts. The development of the equilibria chosen is discussed further in the testing section.

Table 3.14. ΔH values for the equilibrium reactions.

Reactions		ΔH , kJ/mol
$2\text{CrO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$		-23.8
$\text{AcO-H}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{AcO}^-(\text{aq})$		-1.51
$\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \rightleftharpoons \text{CoCl}_4^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$		50.0
$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-$		-30.5
$\text{PrNH}_2(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{PrNH}_3^+(\text{aq}) + \text{OH}^-$		-56.4
$\text{ZnCl}_2(\text{aq}) + 2\text{NaOH}(\text{aq}) \longrightarrow \text{Zn}(\text{OH})_2(\text{s}) + 2\text{NaCl}$		33.1
$\text{Zn}(\text{OH})_2(\text{s}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{Zn}(\text{OH})_3^-(\text{aq})$		-7.1
$\text{NH}_4\text{Cl}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{aq})$		14.8
ΔH_n ranges (neutralization) Strong acids (H^+): HCl or H_2SO_4 , Strong base (OH^-): NaOH Weak acid (HA): AcOH Weak base (B): Na_2CO_3 , NH_3 , PrNH_2 *These values are reported as ranges due to differences in experimental measurements.	$\text{HA}(\text{aq}) + \text{B}(\text{aq}) \rightleftharpoons \text{HB}^+(\text{aq}) + \text{A}^-(\text{aq})$ Weak acid and base	-45.8 to -52
	$\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l})$ Strong acid and base	-56 to -58.3
	$\text{HA}(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{aq}) + \text{A}^-(\text{aq})$ Weak acid and strong base	-52.9 to 54.3
	$\text{H}^+(\text{aq}) + \text{B}(\text{aq}) \rightleftharpoons \text{HB}^+(\text{aq})$ Strong acid and weak base	-47.9 to -51.4

b) Testing: A variety of conditions and chemicals were evaluated to determine the reactions' usefulness in making multi-sensory determinations. The following data are the results of some of the experimental studies performed. The cobalt complex ion equilibrium, which is one of the most popular equilibrium reactions utilized in general chemistry, was examined extensively in order to determine potential chloride sources and additional modifications to allow determination with more than one sense (Table 3.15). The first set of experiments (Test 1) involved monitoring the concentration of the products (CoCl_4^{2-}) and reactants ($\text{Co}(\text{H}_2\text{O})_6^{2+}$) by color changes and the degree of these changes by the addition of HCl and H_2O . Na_2CO_3 , although typically not utilized in the general chemistry Le Chatelier's experiments, reacts with $\text{Co}(\text{H}_2\text{O})_6^{2+}$ to give CoCO_3 , hence removing the hydrate from equilibrium and promoting the reaction to regenerate $\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq})$.

Eleven chloride sources were explored (examples shown in Table 3.15) (tests 2-4) to determine the best reagent for the reaction. Overall the results were dependent on concentration of the salts in the solution, but the extent to which the products were observed at ambient and warm temperatures was dependent on the salt used. The observed trends may be explained by considering mechanisms and/or properties of the salts: lability vs. inertness (lifetime of complex) (56), Irving – William’s series (electrostatic effect of the cation) (57), solubility (58), number of chlorides per mole and/or hydrate vs. anhydrous chlorides (59). Chloride salts such as NH_4Cl and KCl gave no color change at ambient temperature, but when heated the reaction proceeded to the products (blue solution). Anhydrous MgCl_2 and CaCl_2 gave the products to a greater extent at ambient temperature. However, the anhydrous salts created a very exothermic mixture, which may create confusion for students as the ΔH of the cobalt reaction is endothermic. HCl is typically used at high concentrations to promote the formation of the blue cobalt species, as low concentrations of HCl required heating. This may also be attributed to a dehydrating effect of the concentrated acid, in addition to being the source of chloride ions. HCl (6M) was chosen as it did not produce a noticeable increase in temperature (by touch) when added drop-wise to the solution. Similar results for Tests 1 and 2 were obtained from an undergraduate student volunteer and for CaCl_2 in Test 5 when the equilibrium was performed in *iso*-propanol, the solvent used by Van Driel (45). Detailed results for the examination of the chlorides are provided in Appendix D.

These observations may be used as a learning opportunity to explore the properties of the salts. General chemistry students may use tables of dehydrating salts and/or solubilities to correlate the extent that these properties may influence the reaction (sample drying agent table and solubility provided in Appendix D). Additionally, drying agents may be used to make conclusions on the ability to promote the formation of the products in the presence of a chloride source such as dilute HCl (46). Connections to everyday dehydrating substances can be explored such as silica gel packs.

The acid-base and common ion effect equilibria showed potential for using all the senses with little modification. The olfactory determination involved two common aromas to students: vinegar and ammonia (Table 3.16). Typically both of these reactions utilize indicators such as phenolphthalein, methyl red or methyl orange to make visual determinations (43). Indicators were used with these reactions to observe visual changes as a result of pH change and the light probe was used to demonstrate these changes audibly. The beeps observed with the light probe are associated with the change in color of the indicator. Methyl red visually indicates the pH of the solution (concentration of protons). AcO^- and HCl increased the concentration of AcOH (yellow, low H_3O^+) and PrNH_3^+ (red or orange solution, high NH_4^+) respectively. CO_3^{2-} reacts with hydronium ions, which increased the AcOH and PrNH_2 concentrations, further decreasing the pH (high H^+ concentration) and producing a light yellow solution. Additionally, temperature changes as a result of the ΔH (reaction and neutralization) were observed to a greater extent for the dilution of PrNH_2 , as the reagents used were at a higher concentration than with the AcOH .

Table 3.16. Equilibrium that rely primarily on aroma and color changes.

Procedure	Sensorial Observations			
	When	Smell	See	Hear
Acid-Base equilibria $\text{CH}_3(\text{CH}_2)_2\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{CH}_3(\text{CH}_2)_2\text{NH}_3^+(\text{aq}) + \text{OH}^-$				
$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$ added to test tube	Ammonia smell	Clear solution	Rapid beeps (lp) just as with H_2O	Room temp.
Methyl red added	Same smell	Clear to yellow	Slower beeps (lp)	Room temp.
HCl added to sol'n	No smell	Yellow to red	Slower beeps (lp)	Very warm (ΔH_n)
Na_2CO_3 added to tube	Ammonia smell	Red to yellow	A little faster beeps, fizzing	Warm (ΔH_n)
Common ion effect equilibria $\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{CO}_2^-(\text{aq})$				
$\text{CH}_3\text{CO}_2\text{H}(\text{aq})$ added to test tube	Vinegar smell	Sol'n was clear	Rapid beeps (lp) just as with H_2O	Slightly warm
Methyl red added	Same smell	Clear to red	Slower beeps	No change
$\text{CH}_3\text{CO}_2\text{Na}$ added to tube	Smell intensifies	Red to light orange	A little faster beeps than pink solution	No change

Table 3.6. Equilibrium that relies primarily on aroma and color changes (continued).

Na ₂ CO ₃ added to tube	no aroma	Red to yellow	Faster beeps; Fizzing	Warm sol'n (ΔH _n)
H ₂ SO ₄ added to tube	Vinegar smell returns	Yellow to dark red	Slower beeps	Warm sol'n (ΔH _n)

The focal point of the NH₄Cl dissolution equilibrium (solubility) was observation of the physical changes that occur with temperature changes. The dissolution of NH₄Cl is endothermic, therefore warming the solution results in dissolution of salt while cooling allowed the formation of the salt. In order to prevent the entire salt from dissolving in the mixture before heating and cooling steps, a metastable solution was created by dissolving an excess quantity of salt in the water (Table 3.17). The high concentration of the dissolution of NH₄Cl allowed for the very cold temperatures observed even with a lower ΔH than the complexation of Co(H₂O)₆²⁺ with chloride. The optimal conditions for this microscale reaction were ~1g of salt for 10 drops of water.

Table 3.17. Equilibrium with temperature dependence that rely on clarity, sound and temperature changes.

Procedure	Sensorial Observations		
	When	See	Hear
Solubility equilibria (with temperature dependence) $\text{NH}_4\text{Cl}_{(s)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{NH}_4\text{Cl}_{(aq)}$			
H ₂ O added to NH ₄ Cl	Small amount of salt crystals dissolved	Extremely slow beeps (lp)	Got very cold
solution heated	Salt completely dissolved	Rapid beeps (lp)	Not observed*
solution cooled	Salt crystallizes	Slower beeps (lp)	Not observed*

* Hot or cold bath prevents observation by touch.

The Zn(OH)₂ and CrO₄²⁻ equilibria required modifications to make multi-sensory observations, however, the olfactory observations were not incorporated because the reagents used in these equilibria did not present or allowed for olfactory changes. As expected, the solubility of ZnCl₂ to form hydroxozincate ion through Zn(OH)_{2(aq)} intermediate required drop-wise addition of OH⁻ and HCl to observe solubility changes (Table 3.18). A color change was observed with the addition of H⁺ to CrO₄²⁻ (yellow) gave Cr₂O₇²⁻ (dark orange). Na₂CO₃ was used to react this base with H⁺ in order to

observation of color change (visual/light probe), temperature changes (ΔH_n , touch) and fizzing (sound). Both equilibria were easily observed using the light probe introducing sound in the equilibria, even with distinguishing between shades of yellow and orange of the chromate and clarity of the zinc solution. The concentrations of $ZnCl_2$ and NaOH were relatively low, preventing the observation of temperature changes for $ZnCl_2$ to $Zn(OH)_2$ and $Zn(OH)_2$ to $Zn(OH)_3^-$. However, reagent concentrations of CrO_4^{2-} - $Cr_2O_7^{2-}$ equilibrium (placed in the hood) allowed for the experience of temperature changes. The final equilibria students explore give similar results as those already discussed.

Table 3.18. Solubility and chromate equilibria reactions that rely on clarity, sound and temperature changes.

Procedure	Sensorial Observations		
<i>When</i>	<i>See</i>	<i>Hear</i>	<i>Feel</i>
Solubility equilibria $ZnCl_{2(aq)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_{2(s)} + 2Cl^-_{(aq)}$ $Zn(OH)_{2(s)} + OH^-_{(aq)} \rightleftharpoons Zn(OH)_3^-_{(aq)}$			
NaOH added to $ZnCl_2$ sol'n	White ppt formed	Slow beeps sound (lp)	Room temp.
Further NaOH added tube	ppt dissolved	Faster beeps sound (lp)	No change
HCl added tube	White ppt formed	Slower beeps (lp)	Warm [ΔH_n]
Chromate-Dichromate equilibria $2CrO_4^{2-}_{(aq)} + 2H^+_{(aq)} \rightleftharpoons Cr_2O_7^{2-}_{(aq)} + H_2O_{(l)}$			
CrO_4^{2-} sol'n added to tube	Yellow sol'n	Fast beeps (lp)	Room temp.
H_2SO_4 added to tube	Yellow to orange	Slower beeps (lp)	Warmer sol'n
H_2O added to tube	Sol'n lightens	Beeps slightly intensify	Room temp.
Na_2CO_3 added to tube	Light orange to yellow	Beeps intensify(lp); Fizzing	Slightly warm [ΔH_n]

c) *Safety issues*: Since students were using sight, touch, smell and hearing to make observations, safety challenges similar to those of the qualitative organic analysis experiment were faced. Students must discover on their own how to affect the equilibria with minimal guidance, so safety issues must specifically address this designed-based inquiry experience. The equilibria were separated into stations to prevent the limitless variations on the reactions that could occur and

prevent reactions between incompatible chemicals. The stations were also set-up with enough distance between stations so that chemicals were not accidentally or intentionally moved. There were a variety of very different reactions and each station's chemicals were disposed of individually by placing waste containers at each equilibrium station.

The pedagogical goals of the Le Chatelier's experiment were used in the development of LLR. To develop the LLR with these specific pedagogical goals, various considerations were made:

- a) Review of the literature on common equilibrium and LCP misconceptions.
- b) Evaluation of suggestions and interventions to address the misconceptions.
- c) Development of interventions for common learning issues.
- d) Development of conceptual questions to evaluate students understanding of equilibrium.

Equilibrium LLR Pedagogical Objectives

The following learning objectives (Table 3.19) specific to this experiment were developed to align with the M&K thinking systems and mental operations (Chapter 2) and structured around the format of the LLR. The systems and highest mental operations necessary for each objective are specified to demonstrate the cognitive skills required of the students, however the lower cognitive levels are necessary to achieve these skills (hierarchical nature M&K).

Table 3.19. Equilibrium LLR pedagogical objectives and assessments.

Objectives:	Assessed/observed by:	Mental operations:
Students will conduct an investigation of equilibrium reactions by monitoring changes that can manifest sensorially. <i>Systems:</i> Metacognition and knowledge utilization.	a) Establishment and monitoring of goals with logical procedures. b) Development and test hypothesis about the concentration changes. c) Investigate multi-sensory observations.	Experimenting, investigating, specifying goals and monitoring processes.
Students will demonstrate understanding, make generalizations and draw conclusions about LCP. <i>Systems:</i> Comprehension, knowledge utilization, analysis and metacognition.	a) Explanation of the perturbation on the reactions' concentrations. b) Make generalizations and produce definitions about equilibrium and LCP. c) Develop questions and reasonable answers.	Integrating, symbolizing, making decisions, monitoring clarity, and generalizing.
Students will solve problems utilizing the data obtained in the experiment <i>Systems:</i> Knowledge utilization and retrieval.	a) Recognize the thermodynamic and kinetics nature of K_{eq} . b) Predictions of concentration changes for additional equilibria. c) Answer conceptual questions correctly and completely.	Recognizing and solving problems.
Students will self-reflect, provide feedback and examine self-efficacy. <i>Systems:</i> Self-system thinking and metacognition.	a) Rationalize results to identify the importance to the concepts. b) Suggest improvements to the experimentation c) Determine the accuracy of the knowledge obtained.	Examining importance, efficacy, monitoring accuracy and process.

Misconceptions, Interventions and Conceptual Question Development

The literature on common misconceptions and relevant interventions was reviewed to develop specific interventions and conceptual questions for the LLR (60,61). The majority of the misconceptions or interventions found in the literature have been applied primarily to lecture courses, and 6 categories emerged. The following is a summary of: a) common misconceptions, b) relevant literature suggestions and interventions, c) developed interventions to specifically address these misconceptions, and d) concept tests that evaluate the effect of these interventions and misconceptions. After implementation of the experiment, the conceptual questions and interventions were modified in response to misunderstandings of the students observed in the experiment.

1-a. Static Process and Sidedness - Chemical equilibrium is thought of as a static, rather than a dynamic process (62,63). In a state of equilibrium, students may believe no reaction is occurring as there is no macroscopically observable net change in concentrations of products and reactants (45). Chiu et al. showed that students have difficulties with changing from a static model (macroscopic representation) to a dynamic model (microscopic), which may be related to how students construct and organize mental models of the behavior and interactions of particles (64). In addition, no discrimination is made between reactions that ‘go to completion’ and reversibility (65,66).

Treating each side of the reaction separately rather than as a whole is sometimes referred to as ‘sidedness’. A prevailing idea is that forward and reverse reactions alternate and exist as distinctly separate events when equilibrium is attained. “Reactions must go to completion then can be reversed” is a misconception related to this static view (65). The left side of the reaction is thought of as operating independently of the right and the term ‘equilibrium position’ is misunderstood to mean the reaction is taking place only with the reactants or only with the products (one side at a time). Le Chatelier’s ‘stress-then-shift logic’ may reinforce this misconception if not applied correctly (60,65-67) and is related to the misunderstanding on the co-existence of reactants and products.

1-b. *Literature Suggestions and Interventions:*

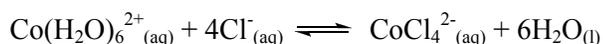
- a) Huddle suggests the use of concrete analogies and caution against analogies such as see saws and mechanical balances as they promote a static view of equilibrium (68).
- b) Van Driel et al. suggest addressing explicitly the chemical changes that are occurring in equilibrium reactions even when there are no observable changes. These authors also used the cobalt chloride equilibrium reaction to explain dynamic equilibrium and incomplete conversion using prompting questions (45). Van Driel et al. suggest tackling these dynamic equilibrium and ‘sidedness’ misconceptions directly in their instruction, rather than just discussing the terminology.

They state that the way to help combat this misconception is for instructors to address the fact that at equilibrium, chemical reactions take place simultaneously (45).

c) Various demonstrations, activities and computer programs have been reported that aid students in learning dynamic equilibrium such as ‘Counting Equilibrium’ (69), ‘BG system’ (70,) other equilibrium demonstration activities using coins, cards and dice (67,71,72) and computer simulation of the forward and reverse rate of an equilibrium reaction ()).

1-c,d. Developed Intervention and Testing :

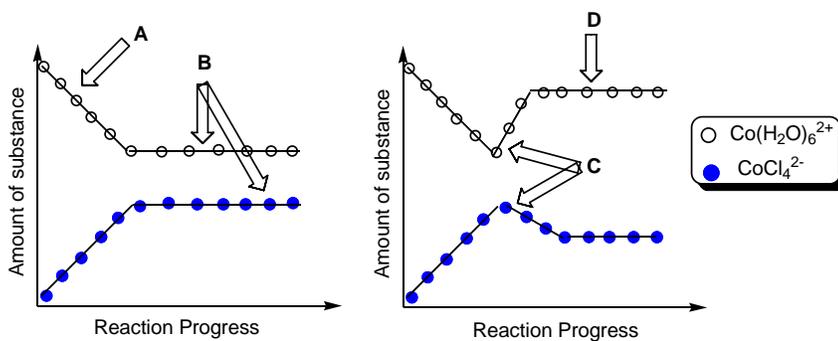
i) The cobalt complex ion equilibrium (Part B) was used to demonstrate the dynamic process by examining reversibility (changing between deep blue and light pink), incompleteness of the reaction (purple) (45), and that both product and reactants co-exist in the flask (purple).



Students were asked to add reagents drop-wise and observe that not only the reactant ($\text{Co}(\text{H}_2\text{O})_6^{2+}$ - pink) or only the product (CoCl_4^{2-} - blue) exist at any given moment, but both co-exist at various concentrations. Students observed that the reaction goes from pink through purple to blue and vice versa, where the changing shades represents different extents to which the forward and reverse reactions occur (Post-lab question 1). Post-lab questions 2 and 3 were developed to test the conceptual understanding of dynamic equilibrium by examining how experimental data correspond to the areas labeled on the graphs (Graph 3.2) and question 3 specifically asked to draw concentration vs. reaction progress graphs for the dichromate-chromate reaction.

Post-lab Question 1: How could you determine the extent of this reaction (degree of formation of reactants and products) and when dynamic equilibrium is taking place (based on your data)?

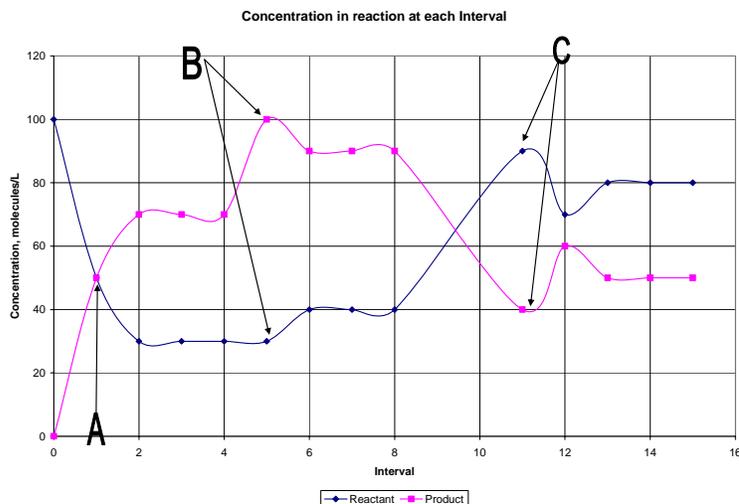
Post-lab Question 2: Explain what was occurring in the test tube depicted in the graphs at the areas labeled A-D in the reaction, and discuss the changes in [prod] and [react].



Graph 3.2. Graph depicting disturbances (A-D) in the complex ion equilibrium.

Post-lab Question 3: Draw *concentration vs. reaction progress graphs* to represent your observations. Indicate on your graph what is occurring in the test tube (chromate-dichromate equilibrium).

ii) An interactive activity, combined the ‘Counting equilibrium’ and ‘BG system’ demonstrations, was developed to exhibit a dynamic equilibrium reaction process and use of correct terminology. The activity requires a group of students to actively represent both products and reactants moving constantly but randomly around in a make-believe flask. Various reaction conditions are observed to demonstrate the extent to which the forward and reverse reactions occur (comprehension – symbolizing). Students take a “snap shot” of the reaction (freeze time) to count the molecules at specific intervals, but it is emphasized that in reality molecules can’t freeze (student can not pause the reaction). The activity serves to prevent students from thinking only one side of the reaction is in motion at a time as well as only products or only reactants being present at any moment. The activity removes the ‘moving to one side or the other’ or ‘pendulum-like idea’ with the random motion in the “reaction flask”. The results are graphed to demonstrate changing concentrations that occur even though there is no net change in the reaction (Graph 3.3, with lines representing a visual guide). This tool has not yet been implemented; however the activity, handouts and instructor’s notes are provided in Appendix D.



Graph 3.3. Representative pre-lab activity concentration vs. interval/time graph.

The arrows B and C correspond to disturbances in the equilibrium and arrow A shows the concentration increase and decrease of the products and reactants respectively.

2-a. Rate vs. extent of the reaction – Equilibrium is most often misunderstood as how fast a reaction proceeds compared to the extent of the reaction’s progress (67,74). Students may think that equilibrium reactions are simple forward reactions, rather than complex mechanisms with a rate determining step (75). The kinetics of reactions are usually not studied at equilibrium (76) and reactions with multiple stable reaction steps require complex calculations (77). At equilibrium (constant temperature), the $rate_f = rate_r$ (no net changes) and $K_{eq} = k_f/k_r$ (thermodynamic equilibrium constant), where $rate_f = k_f[\text{reactants}]$ and $rate_r = k_r[\text{products}]$ (78). The equilibrium and K_{eq} depend on thermodynamics principles as it is related to ΔG and dependent on temperature (79). When the equilibrium is disturbed by changing the temperature, the ratio of the rate constants would change, hence affecting the value of K_{eq} . At constant temperature, the concentrations changes in order to maintain a constant ratio (78). Nevertheless, the concept of the overall rate of the reaction (kinetics) may sometimes be confused with the extent of the reaction. The problem lies with the students’ inability to make a distinction between kinetics (rate of the reaction) and thermodynamics (energy

and transformations) (80,81). The literature shows that many educators prefer a more kinetic (rates) approach (82) to equilibrium problems. The quantitative kinetic approach is thought to be a satisfactory method to determine equilibrium shift based on the equation $k_f/k_r = K_{eq}$, which if explained incorrectly, may lead to misconceptions concerning the extent (74). Other references show a purely qualitative thermodynamic approach (83,84) to counteract equilibrium misconceptions. K_{eq} depends on thermodynamic principles and can be related to temperature and Gibbs free energy, whereas using *only* k_f and k_r may lead students to the concept of dependence on time (rate).

2-b. Literature Suggestions and Interventions:

a) Hansen has developed a physical model that demonstrates thermodynamic changes, kinetics, equilibrium, and LCP using the flow of water between beakers when pouring water from one beaker to another to represent the components of an exothermic chemical reaction and the flow and quantity of thermal energy involved in chemical changes (80).

b) Both thermodynamic approaches (81, 83,84) and kinetics approaches (82,74) have been suggested to reduce the misconception on rate vs. extent. However, both sides of this issue indicate flaws with the other.

2-c,d. Developed Intervention and Testing:

i) The pre-lab activity included basic thermodynamic calculations of K_{eq} . Students are asked to draw concentration vs. time graphs and then correlate this information to the experiment (Graph 3.3). Students associate concentration and temperature changes with the effect on the thermodynamic equations in order to understand the rationale for the change in the equilibrium.

ii) k_f and k_r (kinetic approach) are defined during the pre-lab activity when the students are able to relate them to their qualitative observations (83,84). However, when utilizing k_f and k_r , the term “conversion” is used rather than the use of “rate” or any other kinetics terminology.

iii) A pre-lab question was developed (after implementation) that asks students to draw the extent of condensation and evaporation at equilibrium in a jar when cooled or heated to pictorially represent the dynamic process using LCP. These three interventions make connections between the LCP, the thermodynamic approach and kinetics approach to understand chemical equilibrium.

Pre-lab Question 2: You are given a closed jar containing a blue liquid and observe the liquid evaporates making the air in the jar *saturated* (increased concentration) with a blue vapor above the liquid. You observe that the vapor condenses on the top of the jar and drips back into the liquid. You cleverly manipulate the *extent* of these observations by warming or cooling the jar and observe that at a certain constant temperature no more changes occur. However, your instructor tells you that the *extent of evaporation is now equal to the extent of condensation!* Based on these data, in your own words, define dynamic equilibrium. Draw diagrams to represent molecularly what happens in the closed jar at dynamic equilibrium.

3-a. Physical vs. Chemical equilibrium – Students confuse physical and chemical changes leading to the misinterpretation of physical or chemical equilibria (85). There is a tendency to apply macroscopic properties to the molecular level, for example using melting to mean dissolving. This may be due to a difficulty relating symbolic representation at the microscopic level. This misconception may occur when the making and breaking bonds is confused with just moving atoms around in the equation and cause the inability to relate sensorial changes (macroscopic) to microscopic changes (86). This misconception was observed during the implementation and addressed by the modification of the pre- and post lab questions.

3-b. Literature Suggestions and Interventions:

a) Seffel believes that for students to understand chemistry and the microscopic level, they must first understand what is occurring at the macroscopic level. She has developed an experiment for students to develop definitions for chemical and physical changes through macroscopic changes (87).

b) Various authors have suggested that word association and pictorial representation aid understanding of the macroscopic and microscopic level (67,81). Gussarsky and Gorodetsky used word associations to show advancement in cognitive development in regards to chemical equilibrium. They also suggest that word associations can be a useful tool to reveal and interpret difficulties of students' understanding of scientific concepts (88).

3-c,d. Developed Intervention and Testing:

i) Physical and chemical equilibria are described using a list of words (matching) to evaluate students' understanding of these macroscopic and microscopic terms (Pre-lab question 2). The students are asked to depict pictorially various changes (molecular and macroscopic levels) from a list and then asked to classify the items according to chemical or physical changes (Pre-lab question 3). The inclusion of pictorial representations in the post laboratory questions are used to allow students to contemplate the reactions on both the microscopic and macroscopic levels during the experiment (67,81). These questions prompt students to define physical and chemical changes, as well as promote an understanding of the reactions at the molecular level. Based on their drawings, students are asked to define clearer the physical and chemical changes. Students are asked (modified pre-lab) to relate physical and chemical changes to equilibrium terminology (Pre-lab Question 4).

Pre-lab Question 2: Classify the following words/phases into either chemical or physical change: sublimation, dissolve salt, neutralize acid, melt ice, crystallization, evaporation, cooking egg, condensation, boil water, burn toast, nail rusting, freeze liquid, and souring milk.

Pre-lab Question 3: Choose one item from each group; depict pictorially the transformation occurring at the molecular and explain the change. Discuss what distinguishes the classification.

Pre-lab Question 4: Draw a concept map linking the following terms to chemical and physical changes and include the following words: equilibrium, reversible, temperature,

substance change, molecular reaction, irreversible, reactants, bond making, intermolecular forces, phase change, state. (Students are given a concept map in another question prior to this question as an example.)

4-a. Terminology – Terms used to explain dynamic equilibrium and LCP such as ‘shift’, ‘to the left/right side’, forward or reverse rate, ‘balanced’, and ‘goes to completion’, may cause confusion or support misconceptions (63,65,83). Inaccurate analogies may lead to issues with terminology such as thinking of chemical equilibrium as equilibrium in nature/life, viewing it as a mental balance, weighing balance, applying ‘stress’ in non-chemistry situations (6,66,81,88), see-saw, and a swinging pendulum (65). A closed system may be confused with sealed/closed container (66), rather than one in which mass is conserved, but energy may be transferred.

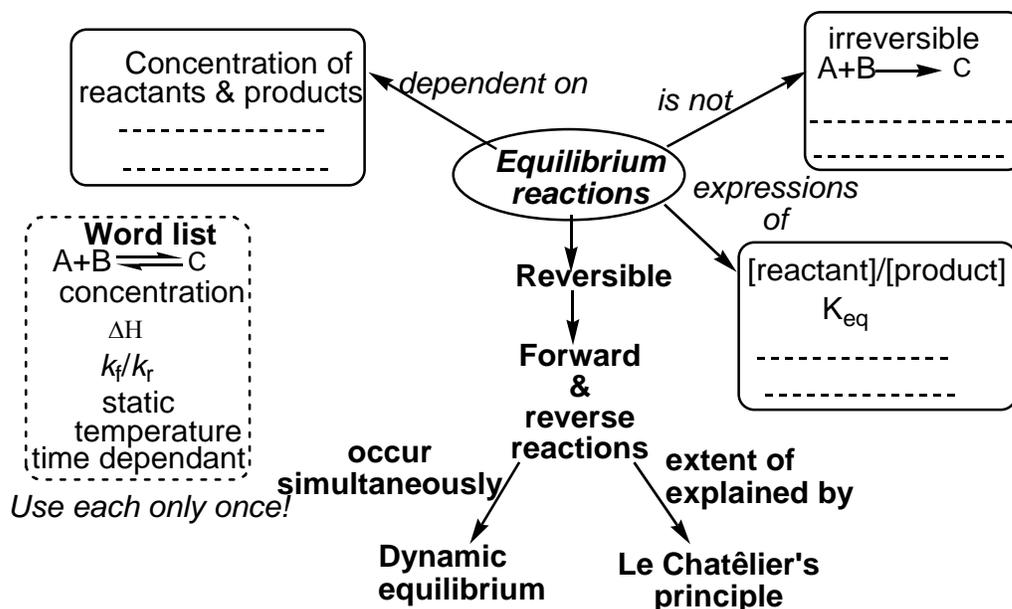
4-b. Literature Suggestions and Interventions:

- a) Bergquist and Heikkinen discuss inappropriate use of language and demonstrate that students’ ideas of terms do not always correlate to correct meanings. They suggest letting students verbalize concepts in order to identify and address misconceptions related to areas such as concentrations, appearance and disappearance of material and the use of the LCP (65).
- b) Tyson et al. stated that language is fundamental to students’ understanding of equilibrium and may be worthwhile removing or clarifying questionable terms such as “shift to right/left”, closed system as applicable to both a sealed container and open beaker, and equilibrium position. They suggest students and instructors work together to decide on the correct meanings of these terms (66).
- c) Gussarsky and Gorodetsky suggest using clear distinctive concepts with no abbreviations for difficult terms and separating everyday events as distinct from chemical equilibrium (88). They used word associations as a graphical representation to link concepts and used this method to evaluate students’ conceptual understanding.

d) Huddle and Pillay suggest the use of concrete analogies which directly relate to items being described (89) such as a game developed by Huddle and Ncube (68). Caldwell, Garritz, and Olney illustrate different analogies for equilibrium such as a dance hall showing LCP, beehive to represent establishing equilibrium, a boy walking down on an up escalator (representing dynamic equilibrium), and painter and sponger who add and remove line of paint to demonstrate constant motion (90).

4-c,d. Developed Intervention and Testing:

i) The use of ambiguous terms and confusing everyday terms, such as shift to the right/left, rate, equilibrium position and pendulums and see-saws, was discontinued or clarified in instruction and questions. Major focus was placed on terminology that expressed change in concentration of the reactants and products. It is vital that students learn how to actively use them through the correct use by the instructor. The position of the equilibrium was determined by forward or reverse processes dominating and the resulting concentrations. A modified concept map allows students to relate equilibrium terminology (Scheme 3.4).



Scheme 3.4. Equilibrium terminology map.

ii) This collaborative inquiry format also allowed students to discuss concepts among themselves to strengthen use of terminology by the communal thought. However, it is important to note that instructors need to emphasize the new terminology, suggest reasons why everyday terms may provide misconceptions and must be careful and vigilant even when using the revised terminology, otherwise inaccurate terms may still be used in the laboratory and on reports (as seen during the implementation of this experiment).

5-a. Concentration – Students assume stoichiometric mole ratios apply to concentrations of products and reactants at equilibrium where stoichiometric moles of reactants and products are equal, or the addition of reactant only affects concentration of product (60). Wheeler and Kass' study found that students were unable to distinguish between concepts of mass and concentrations (74). Gage found that students were able to conclude changes in concentration of one reactant, but were unable to decide what occurs with the other concentrations of substances in the reactions. There was a common belief among students that the concentration of reactants must equal concentration of products at equilibrium and the concentrations fluctuate as equilibrium is established (91).

5-b. *Literature Suggestions and Interventions:*

- a) Gage suggests using developed algorithms to solve problems with K_{eq} aiding students understanding of concentrations and developed a solution model for students to use as reference (91).
- b) Wheeler and Kaas suggest that the use of graphical representations (concentration vs. time) in conjunction with the teaching of the concepts help students visualize concretely the processes in the reaction as well as observe how the concentration of the products and reactants change (74).
- c) Tyson et al. suggest that test questions be framed around changes in concentration rather than shifts (66).

5-c,d. *Developed Intervention and Testing:*

i) The pre-lab activity (discussed previously) uses K_{eq} and concentration correlations (Graph 3.3) to make qualitative justifications for LCP as well as to rationalize the effects observed in the reaction through conceptual questions.

ii) The term “shift” was replaced in all documentation with emphasis on the changes in concentrations of the reactants and products as described previously (post-lab questions 2 and 3).

6-a. Factors and Conditions – Students express doubt on how temperature, volume, or pressure changes adjust the equilibrium concentrations (67,92). Students may think that temperature affects both endothermic and exothermic reactions or forward and reverse reactions in the same manner (93,94). Students may not rationalize that to correctly explain the observed changes for one factor, other conditions should be held constant i.e. students are unable to consider how all factors would affect the equilibrium at once (45,74,95). Particularly the control of variables in relation to gaseous reagents or addition of solids may present problems when considering temperature, pressure and volume. General chemistry textbooks tend to use the LCP and K_{eq} expression, without explicitly controlling the variables and presented as an “infallible principle without limitations” (positivistic claim) (95).

6-b. Literature Suggestions and Interventions

a) Thermodynamics is used to aid in the understanding of temperature effects on equilibrium (81,96). Mahan presented a quantitative experiment using the solubility equilibrium and cooling curves of naphthalene to demonstrate the linear relationship of K_{eq} with temperature (97).

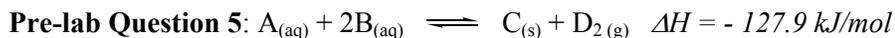
b) Johnstone et al. suggest putting emphasis on the qualitative limitations of the LCP or using only the equilibrium constant expressions (60).

c) Wheeler and Kaas suggested that the limited number of equilibrium reactions encountered by students leads to students' inability to utilize the LCP correctly and rationalize the factors affecting the reactions. They suggest a sample of equilibrium reactions (74).

d) Cheung studied how the LCP adversely affects teachers' ability to solve chemical equilibrium problems and suggests using the reaction quotient (Q_c) to solve these problems (98).

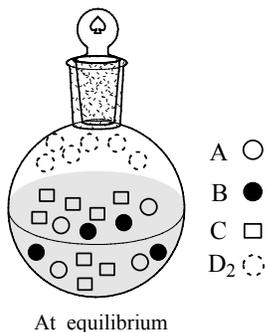
6-c,d. Developed Intervention and Testing

i) Pre-lab Questions 5 and 6 required students to consider the reaction at a molecular level in order to demonstrate the effect of temperature on both forward and reverse reactions (93,96). The dissolution of NH_4Cl and cobalt complex equilibria demonstrated the effect of temperature on the reaction and were explored further through the post lab questions (Post-lab Questions 1, 4 and 5) (97,99). Reactions were selected to demonstrate how temperature affects the forward and reverse reactions as a result of the sign of the ΔH (94).



What will be the overall effect on the concentrations (of products or reactants) when the

reaction is allowed to *re-achieve equilibrium* if:

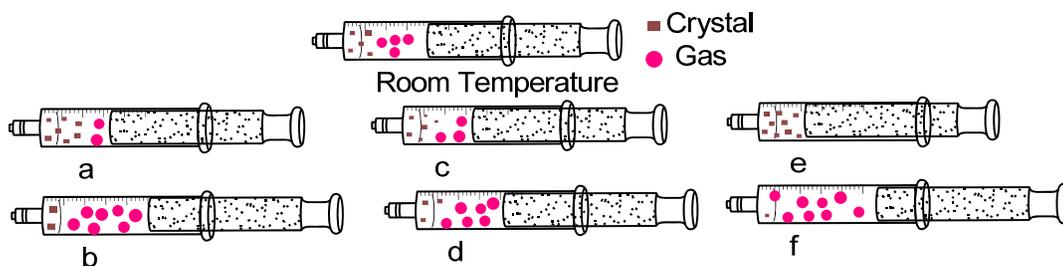


- a) gas D_2 is burned
- b) HCl is added to the system and HCl reacts with B
- c) C is filtered out of the system
- d) the temperature is increased

Demonstrate each change pictorially.

Pre-lab Question 6: Brown crystals are heated in a closed syringe and sublimates to a pink gas that pushes against the plunger. The gas is cooled causing crystals to reform. When left to reach room temperature, both crystals and gas are observed with no observable changes occurring.

- i) Write an equilibrium equation representing the description.
- ii) Choose all possible scenarios that result from decreasing the volume, i.e. pressing the plunger.



Post-lab Question 4: You are given the following in a *closed syringe*: $\text{N}_2\text{O}_4(\text{g}) + \Delta \rightleftharpoons 2\text{NO}_2(\text{g})$

- i) What factors (inside and outside) would disrupt the equilibrium and to what extent would [prod] and [react] be affected by each?
- ii) N_2O_4 is a colorless gas, and NO_2 is brown. What would you observe with these factors, and how can you determine experimentally that equilibrium has been established? Explain your answers using diagrams and graphs to represent what is taking place in the syringe.
- iii) What do you expect will happen if you pulled the plunger of the syringe and increased the volume inside? You have any compound or instrument available to you.
- ii) Six types of equilibria are used to explore a variety of factors and include acid-base, solubility (chemical and physical changes), common ion effect, complex ion and CrO_4^{2-} - $\text{Cr}_2\text{O}_7^{2-}$ - equilibria,. Students used diagrams to rationalize changes to the equilibrium (Pre-lab Question 5 and 6). The reactions are also aqueous which allows for the use of LCP as a predictor of concentration changes.
- iii) Correlation between K_{eq} and temperature are expressed during the pre-lab intervention activity where students see the change in K_{eq} as the temperature was changed. K_{eq} can be correlated to pressure, temperature and Gibbs free energy and to observe a particular factor the remaining factors must be held constant (79,94). Students will use pre and post-lab questions to draw conclusions about the factors affecting equilibrium reaction using the equation $\Delta H/T = -RK_{\text{eq}} + \Delta S$ to correlate K_{eq}

with the changes in temperature due to the ΔH . Students should observe that when ΔH is negative, K_{eq} increases as T decreases and when ΔH is positive, K_{eq} increases as T increases (79).

iv) For future implementation, reaction quotient (Q_c) and/or equilibrium law (K_c and K_p) should be used in conjunction with the predictors of the LCP. These methods should particularly be used for Pre-lab question 6 and post-lab question 4, which involved the generation of gases in a closed syringe. The concentration changes associated with the volume of gases, particularly those in a closed system, can not always accurately be explained by the LCP (particularly when temperature, volume and pressure are not controlled), but can be better explained using Q_c where :

$K_{eq} > Q_c$ - reaction proceeds forward, increasing the concentration of the products.

$K_{eq} < Q_c$ - reaction proceeds in the reverse direction, increasing the concentration of the reactants.

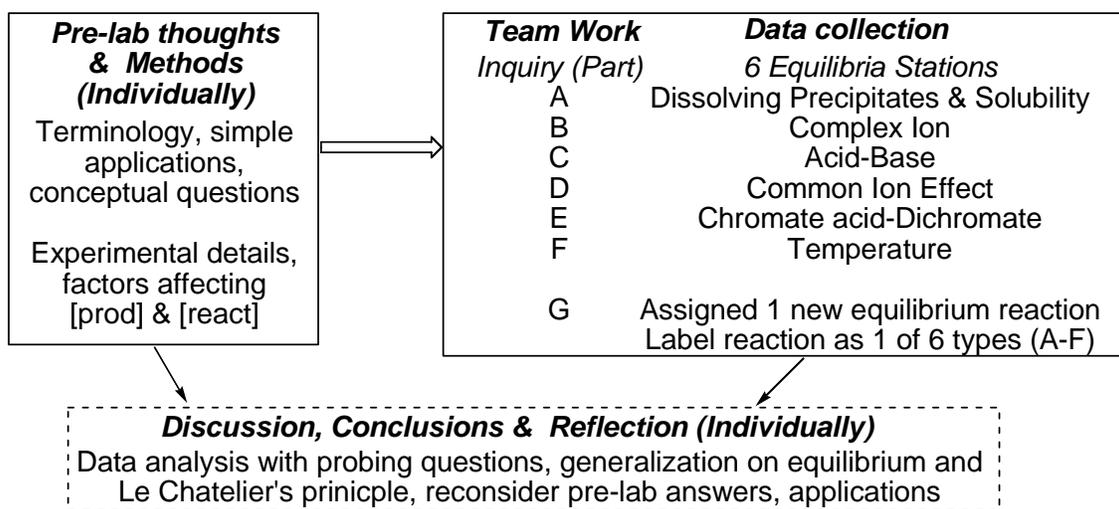
$K_{eq} = Q_c$ then the system is already at equilibrium.

LCP is also limited to qualitative information, while Q_c gives a more quantitative predictor of the concentration changes. However, since Q_c is not covered until the second semester of general chemistry, first semester students can rationalize their results LCP and the differences in results can be a point of discussion for the second semester course.

Unlike the previous sensorial experiments, the researcher did not supervise the students. Instead, the main function was to observe the performance of students, determine any resulting issues associated with the experiment and assist teaching assistants (TAs) in their instruction. Prior to implementing the experiment, the TAs were instructed on the purpose of the experiment and the goals of the LLR. The TAs were required to perform the experiment to ensure they obtained similar results as the researcher enabling TAs to be better prepared to facilitate students' experience.

Implementation Results and Conclusions

This experiment was tested by 45 general chemistry students divided into two concurrent lab sections *before* the topic was discussed in the lecture class. This sensorial experiment was the first to utilize the LLR format, and students were instructed on the expectations for the lab reports. In preparation for the experiment, students were asked conceptual questions related to the experiment (pre-thoughts) and asked to consider how the experiment will be performed (method) in order to start the students thinking about the topic (Scheme 3.5). Students must decide *on their own* what factors affect the equilibria and figure out how the concentrations of the reactants and products change (design-inquiry experience). Minimal guidance was provided, however, students were prompted only when: a) they were uncertain of factors affecting the reaction, b) to inform them of time remaining at each reaction station, and c) issues of safety to prevent accidents during the experiment. The expectations on them for the presentation of their data, complete discussion of each equilibrium reaction and reflection on results and pre-thoughts were discussed during the lab.



Scheme 3.5. Equilibrium LLR experimental components and design.

Students worked collaboratively in groups of 2-3 noting the *extent* of any sensory change. Six different types of equilibrium reactions were set-up as six equilibrium stations with all the necessary reagents and equipment for each reaction provided at its respective station. One station (Inquiry A in Scheme 3.5) consisted of two equilibria, dissolving precipitates and solubility, because of their commonality in reagents. After completing the stations, the groups were provided with an additional equilibrium to explore and classify as one of the previous 6 equilibria types (Scheme 3.5).

Students explored dynamic equilibrium by disturbing the equilibria and observed sensorial changes in each equilibria obtaining similar results to those obtained by the researcher (Table 3.15-Table 3.18). However, students may need to be prompted to utilize *all* the senses and document *all* sensory observations as they are not accustomed to doing so, otherwise conclusions drawn may be incorrect. The revised experimental procedure includes a sample table (similar to those used to present the testing data in Table 3.15-Table 3.18) that separates each sensory observation to prompt students to make and report all sensory observations.

The experimental paths taken by the students and the LLR gave some insights as to the students' understanding of the reactions at the molecular level and their attitudes towards the experimental procedure demonstrated by:

- a) The order in which students added reagents and their explanation of how reagents would affect the reaction demonstrated students' views on the reaction microscopically. For instance, one group added carbonate directly to the amine of the acid-base equilibria (Table 3.16), rather than adding HCl first, therefore the equilibrium was not established prior to adding other reagents.
- b) Some students did not appear to understand what was expected of them at first, but quickly gained an understanding after the first station. A demonstration that explains what is expected of the students without revealing a specific procedure may allow students to think carefully about the reaction prior to starting.

- c) The common ion and acid-base equilibria were the most challenging for students as they had difficulty in deciding which reagents to use and when they were appropriate to be used.
- d) Six students (13%) had difficulty understanding how the affected the concentrations and stated a preference for a detailed experimental procedure as in verification experiments. Others did not have trouble with determining the factors to explore, hence enjoyed the lab or were generally fascinated by their discoveries.
- e) Although several students would have preferred a traditional ‘recipe-like’ format, 16% of students specifically commented that they enjoyed the inquiry aspect of the lab where they were learning and deciding on their own the path to take for each reaction.

Students drew conclusions on the concepts such as specifically relating the concentration of the products and the reactants to the change in equilibrium and the effect of various factors on the equilibria. A rubric was established and used to evaluate and categorize students’ understanding. The students’ answers to the equilibrium questions were classified by the degree of correctness and completeness (C &C, C and N) (Table 3.20). The responses were also characterized as either typical generic text book explanations (lower cognitive responses such as retrieval) or thoughtful analysis (higher cognitive responses such as knowledge utilization). Students utilized the LLR to reflect on the equilibrium concepts to provide these more thoughtful responses after performing the experimentation and having time to reflect on their data (Table 3.21).

Table 3.20. Percentages of student responses characterized by correctness and completeness.

Post-lab Question/Report Section	C&C	C	SC	N
Question 5: Factors that affect: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) + \Delta$. (problem solving and integrating)	42%	33%	18%	7%
Question 6: Definition and critical criteria of common ion effect. (Generalizing and integrating)	60%	20%	9%	11%
Question 7: Definition and use of complex ion. (generalizing)	58%	27%	0%	16%
Conclusion on experiment and LCP (generalizing and decision making, monitoring accuracy)	64%	31%	0%	4%

Table 3.21. Percentages of student responses with thoughtful responses to various questions.

Post-lab Question/Report Section	Percentage of Students
Considered further experimentation, posed questions or hypothesis to further explore equilibrium and suggested other useful reagents that could be used to investigate LCP respect to the equilibrium reactions	44%
Indicated specifically what they had learned from the experiment relative to the concept or what areas they believed they needed clarification (self-system and metacognitive thinking).	49%
Drew correct conclusions about equilibrium concepts and LCP other than simply restating textbook definitions.	33%

However, a few misconceptions and issues were observed from the LLR related primarily to the equilibrium terminology and the understanding of the reaction at the microscopic level. For example the word ‘shift’ (which was hard to eliminate as the term is often used in text books and online) distorted the concept of dynamic equilibrium and the understanding of how the reactants behave. The difference between physical and chemical equilibria also created difficulties for students (addressed in revised experiment). Students’ choice of experimental paths, reflection and conceptual question responses demonstrated inadequacies in their knowledge that may otherwise not be observed through the traditional format and questions. For instance, students had difficulty with ionic equations understanding the use of OH^-/H^+ in the reactions, however, they had not covered acids and bases in their lecture course, so some explanation was necessary to explain these ions and their use in the reactions.

As indicated from the results of the LLR model, the instructors also observed students’ conceptual understanding of the experiment, which then allowed for the modification of pre and post lab questions to address common learning problems (Table 3.22). These changes were discussed in detail in the pedagogical discussion section. Instructors can be better equipped in future implementations to take action *during* the learning process with the information from the LLR and this implementation. The revised experimental procedure incorporating the interventions, rubric,

complete analysis of the points awarded for each section of the experiment and post-lab questions with sample responses are provided in Appendix D. To fully assess students' conceptual understanding, this experiment can be run alongside traditional Le Chatelier's experiments with and without the LLR format as a control in further implementations.

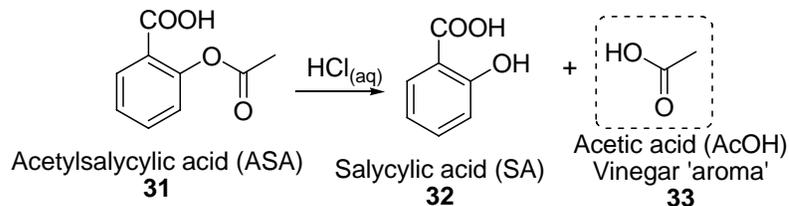
Table 3.22. Problems observed during implementation and interventions to address these.

Problem observed	Developed intervention
<ul style="list-style-type: none"> - Understanding of macroscopic and molecular levels. - Terminology for physical and chemical changes used interchangeably (85). - Example: melt and freeze to represent dissolving and crystallizing. 	Matching physical and chemical changes to terminology and pictorial representations at the microscopic level.
<ul style="list-style-type: none"> - Even with changes in terminology to the procedure and questions, students may still apply terms used. - Students focus on shift to right/left. 	Focus more on terminology used in the activity, experimental procedure, during the lab session by the TAs and conceptual questions.
<ul style="list-style-type: none"> - Coexistent products or only reactants and forward and reverse reactions not understood. - Equilibria must go to completion. 	Interactive activity where students observe constant reactions reagents and products (dynamic equilibrium). Investigate concentration-time graphs.
<ul style="list-style-type: none"> - Rationalization of how equilibria are affected by various factors. - Explanation for changes in equilibria with gaseous reactants and products. - Rate equals extent of the reaction. 	Define LCP and explore dynamic equilibrium using qualitative thermometric and kinetics approaches. Compare and use Q_c with K_{eq} , particularly for gases.

3.4 Acetyl salicylic acid kinetics

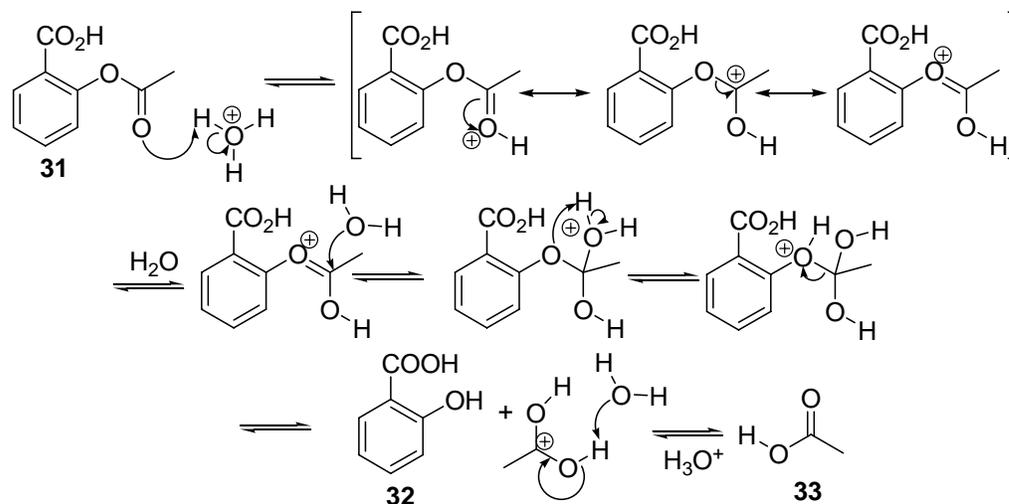
Acetyl salicylic acid (ASA) kinetics is typically studied in undergraduate laboratories spectroscopically by monitoring the changes in concentration of ASA (**31**) (102) or using a UV-Vis spectrometer to monitor the absorbance produced from color intensity due to metal complexation of iron or copper with the salicylic acid (**32**) produced (103). This olfactory experiment utilized the vinegar aroma produced by the reaction to examine the rate of the reaction without the aid of instrumentation. Students observed the vinegar aroma of acetic acid (**33**) (Scheme 3.6), noted the time taken to observe the aroma at various concentrations of ASA ([ASA]) and plotted their data in a

similar manner as experiments performed spectroscopically. Unlike the esterification kinetics experiment (Section 3.2), this quantitative experiment requires the manipulation of data using typical kinetics calculations to determine the rate constant and order.



Scheme 3.6. Hydrolysis of acetyl salicylic acid produces a vinegar aroma from acetic acid.

This bimolecular reaction was studied by using excess aqueous acid, which makes the hydrolysis a pseudo-first order reaction with respect to ASA just as in traditional experiments (Scheme 3.7). The time data taken to observe the vinegar aroma for various [ASA] was determined, tabulated and used to plot the three typical kinetics graphs, [ASA], ln [ASA] and 1/[ASA] vs. time. Unlike the ideal kinetics situations shown in the typical general chemistry textbook problems, students are exposed to a real example in which the typical graphs are not perfectly linear. The graph that best represents the kinetic data is determined by a line of best fit or linear regression (126) using the statistical measure, R^2 . Students cannot simply inspect the shape of the graphs in order to draw conclusions about the order, but must use the R^2 to demonstrate which graph had a straighter line. The rate constant (k) was determined from the slope of the line (m), as the equation of the line ($y=mx+b$) correlates to the rate law equation: $-d[\text{ASA}]/dt = k[\text{ASA}]$ (intercept, $b=0$).



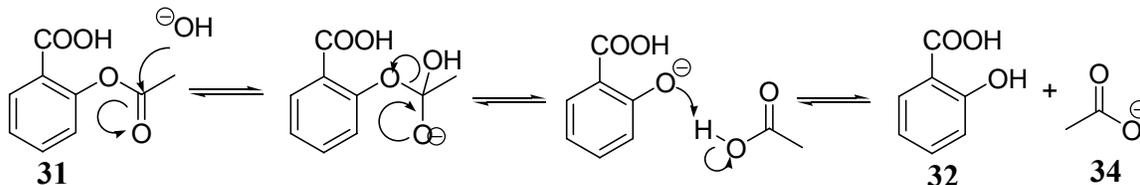
Scheme 3.7. Mechanism of ASA acid-catalyzed hydrolysis.

In order to develop this ASA hydrolysis experiment, a variety of chemical considerations were explored:

- i) Consideration of suitable conditions and quantity of reagents.
- ii) Thorough chemical testing to ensure the experiment was reliable and accurate.
- iii) Safety concerns with regard to observations using the sense of smell.

i) *Conditions and reagents:* Typical ASA hydrolysis experiments use NaOH, while few use HCl to catalyze the reaction. In this experiment the acidic medium was chosen as an alkaline medium would prevent the AcOH aroma (Scheme 3.7) producing instead AcO⁻ (**34**) (Scheme 3.8). The common reaction temperature is approximately 60°C and is often performed in water (102-104) which prevents additional aromas such as salicylic esters from Fisher-transesterifications. The concentration and volume of HCl that would be suitable for the experiment in terms of time necessary for each trial and quantities commonly used (105) were examined. Aspirin tablets were also considered as an alternative to pure ASA. The 300 mg dose Aspirin tablets were relatively close in weight, varying in total weight between 0.371-0.374g. The tablets contain other components such as starch and cellulose which could create competing hydrolysis reactions. Aspirin tablets need to be

crushed, adding an additional step to the procedure. ASA was used in this experiment as it was also relatively inexpensive at 1 kg/\$59.28 from Fisher Scientific (~30 groups) in its pure form and was already in powder form.



Scheme 3.8. Mechanism of ASA base-promoted hydrolysis.

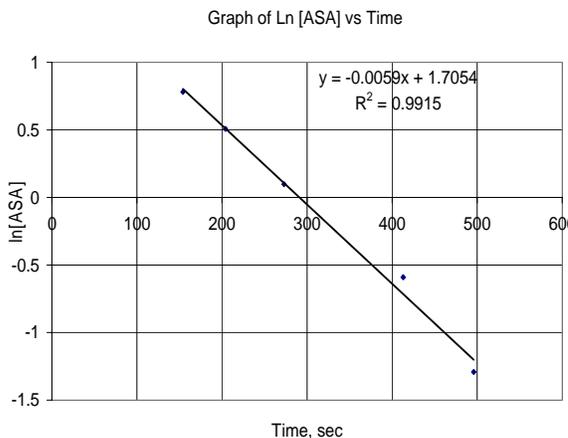
ii) *Testing:* No significant differences were observed with the hydrolysis using HCl, HNO₃ and H₂SO₄ as inorganic acid catalysts, so HCl was chosen due to the availability in most laboratories. The minimal quantity of acid to be used was based on the volume at which the maximum quantity of ASA appeared to completely dissolve at approximately 60°C. Using approximately 2 g of ASA and 20 mL of varying concentrations of HCl solutions (0.1-2 M) as a template, the effect of the concentration on the rate was compared. Solutions of ~1-2 M HCl were considered to provide reasonable reaction times (Table 3.23).

Table 3.23. Effect of HCl concentration on the time for the emergence of the AcOH aroma (3 trials each).

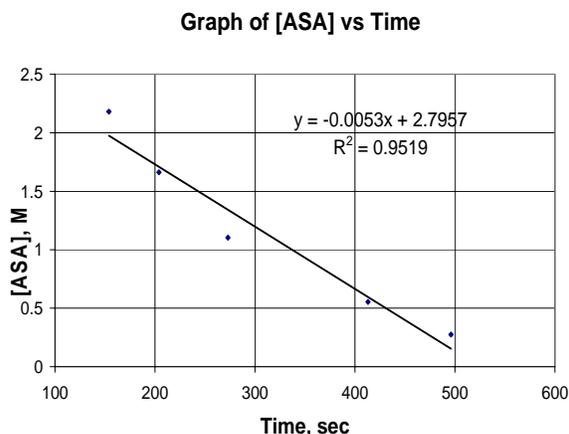
Concentration of HCl, M	Average Mass ASA, g	Average Time, s
0.10	1.989	458
0.25	2.233	437
0.50	2.002	364
0.70	2.013	346
1.00	2.005	281
2.00	2.003	215

The kinetics investigation was conducted under the conditions considered suitable for the undergraduate laboratory (1-5 g of ASA). The research data confirmed a pseudo first order reaction as the graph of the ln[ASA] vs. time gave an average R² value of 0.9675±0.017 where n=6 (Graph

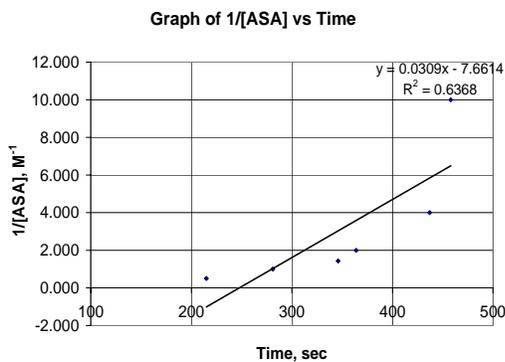
3.4) and average R^2 values of 0.9235 ± 0.029 and 0.7152 ± 0.059 for the $[\text{ASA}]$ and $1/[\text{ASA}]$ vs. time respectively (Graph 3.5 and Graph 3.6).



Graph 3.4. Representative graph of $\ln[\text{ASA}]$ vs. time.



Graph 3.5. Representative graph of $[\text{ASA}]$ vs. time.



Graph 3.6. Representative graph of $1/[\text{ASA}]$ vs. time.

iii) *Safety issues:* AcOH and ASA do not pose a threat to the students except for students allergic to Aspirin. These students were asked to coordinate with their lab partners to prevent exposure to ASA, but still remain active in the entire experimental procedure. The experimental set-up included place-markers taped to the lab bench to demonstrate a reasonable distance between the set-up and the observer (Figure 3.6).

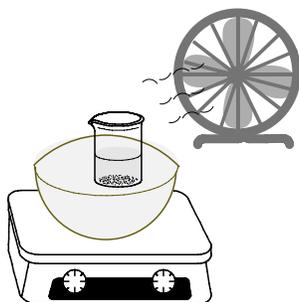


Figure 3.6. Kinetics hydrolysis experimental set-up.

Kinetics LLR Pedagogical Objectives

The pedagogical objectives and assessment of this kinetics experiment were developed using the M&K's mental operations and systems and structured around the format of the LLR (Table 3.24).

Table 3.24. ASA kinetics LLR objectives, assessment and associated cognitive skills.

Objectives:	Assessed/observed by:	Mental operations:
Students will conduct an investigation of ASA hydrolysis kinetics and manipulate the data to determine the rate order and k . <i>Systems:</i> Metacognition and knowledge utilization.	a) Investigation of rate using AcOH aroma to first appear at various concentrations of ASA. b) Monitor olfactory data. c) Examination of kinetics graphs to determine rate order and k .	Experimenting, investigating, and monitoring processes.
Students will demonstrate understanding, make generalizations and draw conclusions about kinetics and rates of reaction. <i>Systems:</i> Comprehension, knowledge utilization, analysis and metacognition.	a) Derive kinetics expressions. b) Explanation of how the graphs were used to find order and k . c) Generalizations about order as it related to the conditions used. d) Develop questions and reasonable answers.	Symbolizing, making decisions, monitoring clarity, and generalizing.
Students will solve problems to draw conclusions about new situations. <i>Systems:</i> Knowledge utilization and retrieval.	a) Recognition and use of correct kinetic expressions in solving problems. b) Predict how an excess of a reagent allowed for pseudo rate order. c) Answer conceptual questions correctly and completely.	Recognizing and solving problems.
Students will self-reflect, provide feedback and examine self-efficacy. <i>Systems:</i> Self-system thinking and metacognition.	a) Rationalize results to identify the importance of the concepts. b) Suggest improvements to the experimentation c) Changes in the re-evaluated pre-lab. d) Utilization of aids provided	Examining importance, efficacy, analyzing errors, monitoring accuracy and process.

Misconceptions, Interventions and Conceptual Question Development

The following are common misconceptions and interventions discussed in the literature that are relevant to this experiment. Based on these misconceptions and guided by the interventions, specific interventions were developed for this ASA kinetics experiment. The summary is divided into: a) common misconceptions on kinetics found in the literature and difficulties with kinetics calculations, b) relevant literature interventions, c) interventions developed to address misconceptions and typical calculation difficulties, and d) conceptual questions to assess understanding. After the experiment was implemented, the conceptual questions were modified to further identify and address learning difficulties observed during the implementation of the experiment. A variety of conceptual questions were developed, which demanded various cognitive levels of thinking. Sample questions are presented, but all questions are provided in Appendix E.

1-a. Rate, equations and graphs – Students may not understand how to make correlations between the graphs and the rate expressions, nor how to derive reaction order and rate constant from the rate expressions (106). Students may not correlate the progress of the reaction or the changes in concentration with the changes in rate (107). Students commonly misunderstand the basis of kinetics or rates of reaction, have difficulty with how temperature affects rate, and do not connect these to collision theory (93). Students may not understand that the rate order is determined by the slow-step of the reaction scheme (108).

1-b. Literature Interventions

a) Reeves explained that calculating overall rate orders leads to misconceptions, rather than clearly defining individual reaction orders with relation to specific compounds (108). Quisenberry and Tellinghuisen suggest that rate orders and k be made unambiguous by explicitly stating the reagents for which they are meant to apply (109).

- b) Mason et al. used energy profiles to demonstrate changes in energy resulting from changes to the reaction being observed and suggest emphasizing the energy changes in the reaction rather than the positions of the levels (110).
- c) Gupta suggests that the use of mechanisms and reaction schemes as interchangeable is misleading. A reaction scheme can be determined by the kinetics, while a mechanism is more detailed requiring further studies (75), therefore the term reaction scheme should be used rather than mechanism when intermediates and reaction specifics are unknown (75). Laidler and Glasstone presented concise and simple definitions of kinetics concepts as well as presented an outline of the basic principles of rate law in response to the high degree of misconception on the topic (111).
- d) Various analogies (112-114), games (115) and activities (113) have been developed to aid the understanding of kinetics concepts. Fortman compares couples having babies with first order kinetics and the effect of concentration and temperature on rates using the analogy of cars in a parking lot (113). Evenson developed a 'dry experiment' that is used to provide concrete analogies of collision theory and the factors that affect reaction rates (114). A game developed uses a dice to demonstrate activation barrier and first order reaction. This game also uses buying or winning chemicals and heat in order to demonstrate the completion of an elementary reaction. (115).
- e) Bergquist and Heikkinen suggest letting students verbalize their concepts in order to identify and address those (65).

1-c. Developed Interventions and Testing

- i) The experiment and questions were phrased around specific reaction schemes or reagents when referring to rate expressions, order and k . Conceptual questions were framed to encourage students to make their own definitions as well as pictorial representations. The experiment can be worded to allow students to relate the rate order to the rate limiting step of the reaction scheme being observed when the detailed mechanism is given. However, first semester students do not understand organic

symbols, so reaction mechanisms may therefore create confusion (Scheme 3.7). An energy profile was used to demonstrate changes in energy resulting from the catalyzed and uncatalyzed ASA hydrolysis (comprehension skills).

ii) Conceptual questions were developed (based on Fortman's analogies) to relate rate to everyday concepts specifically using an analogy of translation between English and "Chemistry" languages (to translate terminology and explain music and dancing (Post-lab Question 1). Students use the questions to guide their derivation of the rate expressions and rate laws in a stepwise manner and connecting reaction expressions to rate order and rate expressions to zero, first and second order rate laws. The questions assessed students' comprehension of the derivations and visualization of kinetic concepts (comprehension and analysis skills).

Post-lab Question 1: Using appropriate chemical terminology and diagrams, you explain ballroom dancing to your friend who only speaks 'Chemistry'. You compare the effect of changing the speed of the music and increasing the number of people to increasing the temperature and concentration in a kinetics reaction respectively. Complete the diagram, and calculate concentrations, time and k to fill in the blanks.

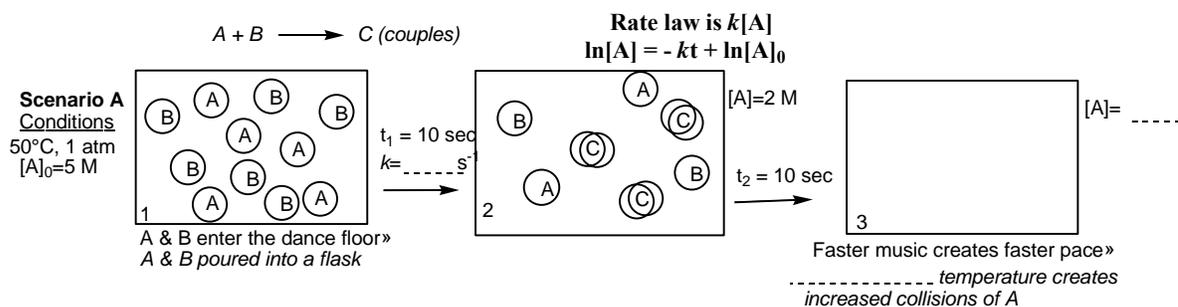


Figure 3.7. Section of kinetics post lab question depicting reaction at the molecular level.

The kinetics graphs and rate equations for zero, first and second order were derived in a simple step-wise manner to utilize the appropriate symbols (symbolizing and integrating) (Pre-lab

Question 1). Students used this derivation to determine the rate order of the reaction, rationalize their decision and derived the correlation between the slope of each graph and the k (Post-lab Question 2).

Pre-lab Question 1:

$$\text{rate} = k[A]^1 = \frac{-\Delta[A]}{\Delta t}$$

1 Simplify

$$= \frac{-\Delta[A]}{\Delta t}$$

2 Rearrange

$$k\Delta t =$$

3 Integrate

$$[k\Delta t = \int \frac{-\Delta[A]}{[A]}$$

$$kt = \int \frac{dx}{x} = \ln x + c$$

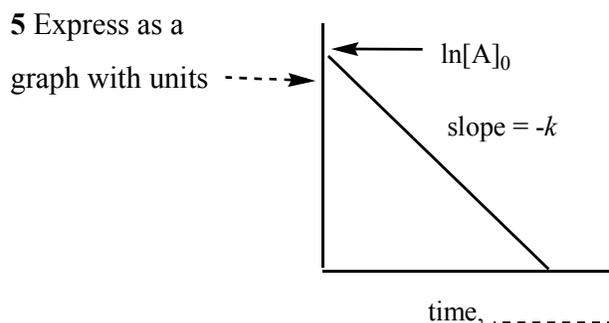


First Order

4 Rearrange to express as a line equation

$$= -k t + \ln[A]_0$$

$$y = m x + c$$



Post-lab Question 2:

Since k is always >0 , based on the integrated rate equations:

Slope:
negative/positive?

For first order, k is the

slope; rate equation:

.....

2-a. Graphs and Calculations

Students may not be able to extract the required information from the graphs or understand the relationship between rate order and the kinetics graphs. The arithmetic relationship between concentration and time for each kinetic graph may pose problems for students (93,116). Students often have problems with the logarithmic scale, which leads to the inability to correctly understand the kinetics graphs (117).

2-b. Literature Interventions

a) DePierro et al. offer approaches to help students overcome the difficulties of translating, manipulating, and interpreting mathematical expressions that contain logarithms. For example, they

suggest having students translating “logarithm” or “antilogarithm” expressions into words/sentences to reinforce the idea that logarithms are exponents (117).

b) Quisenberry and Tellinghuisen suggest students should no longer be sheltered from the minimal amount of calculus required to understand the derivation of the integrated rate laws (109).

c) Sanger et al. had students determine whether burning a candle and flipping pennies are consistent with rate laws. The time-dependent data was collected and plotted curves of amount versus time, $\ln(\text{amount})$ vs. time, and $(\text{amount})^{-1}$ vs. time were used to determine rate constants (118).

2-c,d. Developed Interventions and Testing

i) Sample data allowed students to practice calculations on molarity and logarithm. Using a calculation diagram (Pre-lab Question 2), students determined the areas of the diagram necessary for calculations in Pre-lab Question 3. Students were asked to provide their own scheme or calculations methods, if any.

Pre-lab Question 2:

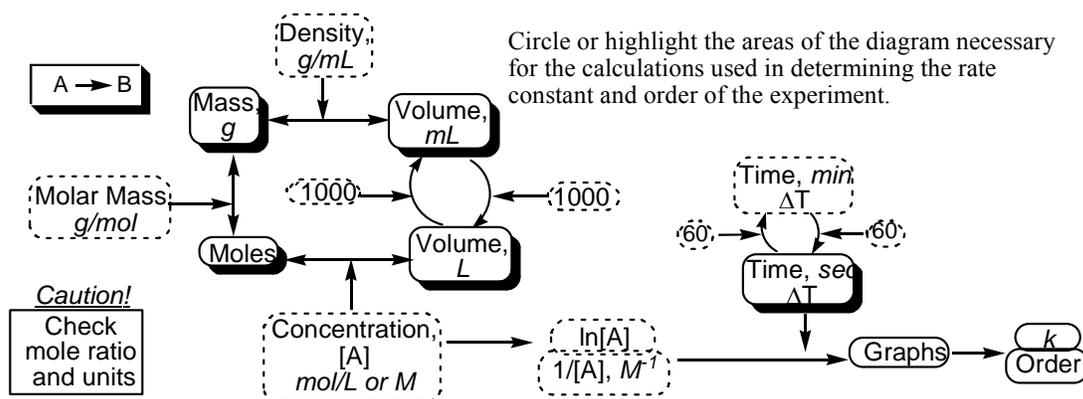


Figure 3.8. Calculation diagram for the ASA kinetics.

Pre-lab Question 3: In a kinetics experiment, you share data with other groups. However, the other groups did not collect data you could trust. Your instructor tells you the data you

collected is enough to complete the table below. Calculate the values to **complete** the table below. You may use the diagram above (refer to Figure 3.8).

A \longrightarrow B					
MM of A =50.0g/mol Volume of a =200.0mL					
Mass of A, g	moles of A	[A], M	ln[A]	1/[A], M ⁻¹	Time, sec
	0.20	1.00	0.00		60
15.00	a	1.50		0.67	50
20.00	b		0.69		40
c	0.50	d		0.40	30

ii) Pre-lab questions focused on deriving the expressions and rate order to make connections to the kinetics graphs (pre-lab question 1). Students briefly explored basic calculus and logarithmic calculations through the step-wise mathematical progression of the rate equations. The post-lab discussion and post-lab questions assessed students' ability to apply graphical relationships (making decisions).

3-a. Molecular level – An understanding of the relationship between symbolic, macroscopic and microscopic levels is essential to the comprehension of chemistry principles and the success in chemistry courses (93,119,120). The inability to visualize solutions and reactions at the molecular and symbolic representation levels creates misconceptions of the kinetics of reaction (121-123). An emphasis on algorithmic problems rather than a conceptual understanding of kinetics and its calculations may create these misconceptions (124).

3-b. Literature Interventions

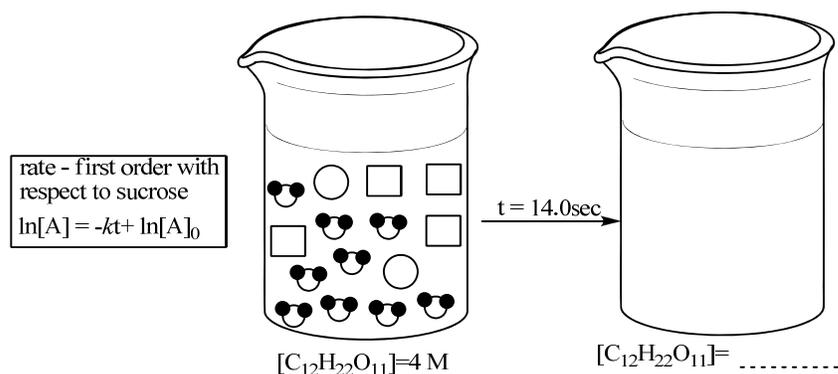
a) Gabel et al. analyzed students' conceptions on the particulate nature of matter using pictorial questions and suggest that an emphasis on this area along with careful representation of particles aid

students understanding, as well as correlation of the microscopic representation at the symbolic level and connection to the macroscopic level (121). Smith and Metz examined the microscopic representations of solutions for undergraduate, graduate and faculty to examine the misconceptions associated with solution chemistry including acids and bases, acid strength, dissociation, diatomic elements, and bonding. They suggest that pictorial representations (visual aids) may increase comprehension and that microscopic representations are useful for evaluating students understanding (124).

3-c,d. Developed Interventions and Testing

a) Pictorial questions were developed to depict reactions at the molecular and macroscopic levels with use of representative symbols and equations (post-lab question 1). Students were not specifically instructed in the lecture portion of the course on the particulate nature of matter. These questions were developed to prompt students to make necessary connections between these three levels through a combination of problem solving and pictorial representations (pre-lab question 4).

Pre-lab Question 4:



4-a. Stoichiometry – Students often hold the misconception that kinetic information can be obtained from the stoichiometric equation (93). Students have the misconception that the stoichiometric coefficients represent the number/amount of molecules in the reaction or the exponents of the rate order expression rather than just demonstrating mole ratio (75). Students often have difficulty in

making typical calculations of mole, concentration and volume, which may be due to the inability to conceptualize or visualize the molecular, symbolic, and graphical representations of chemical phenomena (125).

4-b. Literature Interventions

a) Arasasingham et al. have developed a test designed to follow conceptual development of students understanding of stoichiometry, as well as assess the impact of a Web-based instructional program intervention. The authors used knowledge space theory, which describes the possible states of knowledge to assess students understanding and integration of the molecular, macroscopic, symbolic and graphical levels (125).

b) Gupta suggests distinguishing stoichiometric quantities from orders by specifically discussing the coefficients when relating the reaction, then mentioning the orders specific to the reactants (75).

4-c,d. Developed Interventions and Testing

i) Post-lab question 1 (page 147) required pictorial demonstration of the stoichiometry to prompt students to think about the reaction on a microscopic level. Pre-lab question 5 evaluated students' understanding of the differences between reaction stoichiometry coefficients and rate of reaction exponents.

Pre-lab Question 5: What determines the **exponents** of the rate law? Select the correct response below:

- | | |
|---|----------------------|
| i) experiments | iv) all of the above |
| ii) coefficients in a balanced equation | v) only i and ii |
| iii) initial concentrations of reactants. | |

Implementation Results and Conclusions

The hydrolysis experiment was first performed by 39 first semester (FS) general chemistry students in two concurrent lab sections. FS students used the LLR format throughout the semester and were properly instructed on what was expected. Just as with the equilibrium experiment, the researcher did not supervise the FS students, but made observations about the performance of the students during the implementation, remedy any problems that may arise and assisted the TAs in their instruction. Prior to implementing the experiment, TAs were instructed on the purpose of the experiment and the goals of the LLR. After this implementation, the experiment and questions were modified to address common learning difficulties observed in areas such as derivation of the rate expressions, kinetics graphs and rate order.

The experiment was then performed by 27 second semester (SS) general chemistry students in 3 lab sections (after initial exposure to the concepts in the lecture course). The SS students were only exposed to the LLR format for this one laboratory session. These students used the conceptual questions in the LLR format to construct their laboratory report. Unlike with the previous implementation, the SS students had the same instructors (researcher and lecture TA) in each section. The SS implementation was performed one year after the first implementation and there was only one student who had prior exposure to the original experiment.

Students worked in groups of 2-3 students in the laboratory and monitored the time taken for the vinegar aroma to first appear at various quantities of ASA (1-5 g). Students tabulated their data of mass and time, used these data to calculate $[ASA]$, $\ln [ASA]$ and $1/[ASA]$ and drew kinetics graphs with this information. Students were only given guidelines to perform the experiment, but decided on their own how to utilize their data (based on their answers to pre-lab question 1 and 3). Students evaluated which of the three typical kinetics graphs best represented the kinetic data obtained. Both the FS and SS students correctly identified the pseudo-order of the reaction with

respect to ASA from their graphs where the average for all groups was $R^2 = 0.9452 \pm 0.032$ ($n = 15$ groups).

Some SS questions and tasks were similar to the FS, however others were changed to assess specific issues and interventions conducted in the second semester. From the slope of the line of \ln [ASA] vs. time graph, 56% of FS and 70% of SS students correctly identified k as a positive value between 0.02 and 0.03. The increase in the number of students who correctly identified k as a positive rather than a negative number reflects a positive effect of the changes made to questions on the LLR. SS students were required to derive the kinetics expressions and utilize the expressions to complete conceptual questions, rather than simply reviewing the expressions from the textbook as the FS students had done.

Students' responses to the questions were evaluated and used to infer the effectiveness of the questions, gauge students' understanding of the concepts, and determine implications of the data between the initial responses to the pre-lab questions and their re-evaluated responses. FS pre- and post-lab questions were modified or replaced after the first implementation to better assess students understanding and evaluate the impact of changes made the questions. These questions were then used to evaluate the SS students and new rubric established. Students' responses were coded as the degree of correctness and completeness of the response: correct and complete thoughtful or rationalized responses (C &C), correct but not complete (C), somewhat correct (SC), and neither correct nor complete (N). These assessments provided evidence that both FS and SS students: a) discussed and made determinations from the results (integrating and specifying), b) developed reasonable questions (specifying), c) derived sensible conclusions describing additional experimentation and modifications (making decisions and specify goals), d) made connections and utilized knowledge (problem solving and generalizing, post-lab question 1-3) and, e) reflected on the pre-lab questions (analyzing errors and examine importance) using the LLR (Table 3.25). Students'

reflections on the pre-lab questions demonstrated gains in students understanding of the concepts after performing the experiment as the percentage of C&C and C responses increased between the initial responses and the re-evaluation of their responses. For instance, students were able to derive the rate expressions (question 2) and were better able solve pictorial problems (question 6) after the experiment was performed demonstrated by the changes to their responses (Table 3.25).

Table 3.25. Change in correctness of kinetics responses for pre-lab questions through reflection.

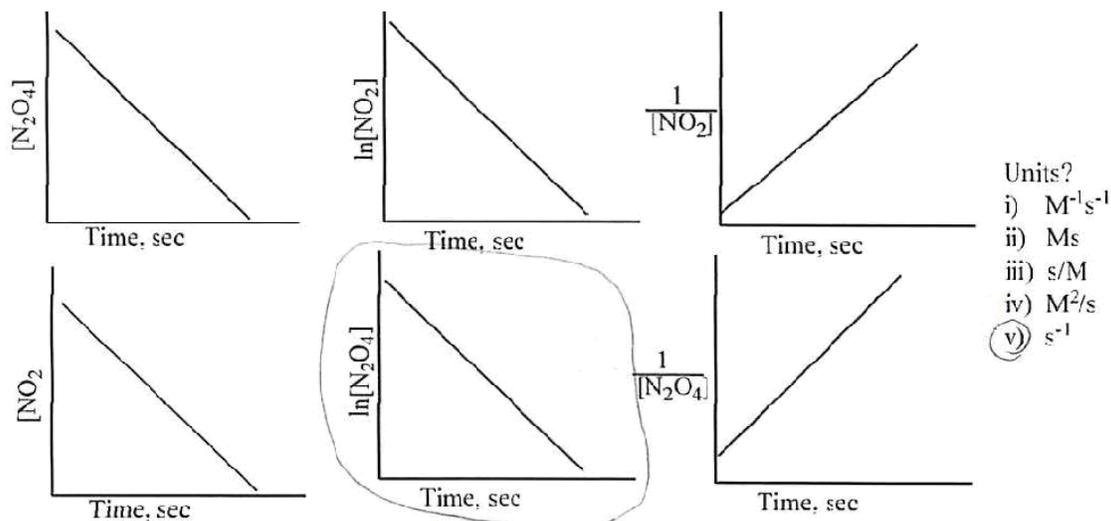
Pre-lab Questions	Initial response				Re-evaluated response			
	C&C	C	SC	N	C&C	C	SC	N
Question 2 – Derive rate expressions (symbolizing)	78%	19%	4%	0%	93%	7%	0%	0%
Derive generic rate expression for ASA hydrolysis (matching and symbolizing)	52%	30%	15%	4%	85%	11%	4%	0%
Question 4 – Determine calculations (diagram) needed to derive k and rate order (metacognitive skill)	19%	30%	48%	4%	63%	19%	19%	0%
Hypothesize experimentation to explore a pseudo order reaction (knowledge utilization and experimenting)	30%	30%	30%	11%	74%	11%	7%	7%
Question 6 – Kinetics diagram and calculations (solving problems)	37%	30%	22%	11%	63%	22%	11%	4%
Determine how rate changes with time (generalizing and experimenting)	26%	44%	19%	11%	52%	37%	0%	11%

For the question below (post-lab question 3), 63-88% of students in each of the three SS lab sections were able to identify the correct graph that represents the information given and determine the units of k . This post-lab question required an extension of the concepts learned as all the graphs had straight lines (rather than having students derive the most linear line) where students must make connections between the equation of the reaction and rate law with the axes of the graphs, then derive the units of k from the selected graph based on the units on the y axis. To answer this question, students must reflect on the derivations of the rate expression made the pre-lab questions, determine how the units are derived from a graph

Post Question 3: For $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$, the rate law is $k[\text{N}_2\text{O}_4]$.

Circle the graph that represents this information with a brief explanation. What are the units of k for the reaction?

C&C response:



Explanation:

The rate law given is $k[\text{N}_2\text{O}_4]^1$, which points to a first order reaction. This produces the equation $\ln[\text{N}_2\text{O}_4]_t = -kt + \ln[\text{N}_2\text{O}_4]_0$ which matches the 4th graph. The units cancel with s^{-1} .

The original implementation revealed shortfalls in their knowledge of kinetics concepts. These included treating stoichiometric coefficients as exponents and inability to manipulate data to determine the rate order and k from the kinetics graph. Pre and post lab FS questions were then modified and implemented with SS students to address these misconceptions and to evaluate understanding of the reaction at the particulate, macroscopic and symbolic levels through drawing diagrams. A revised pre-lab question was given that specifically evaluate this problem in the SS and prompt students to consider the difference between coefficients of the equation and exponents of the rate expression. It was observed that SS students continued to confuse these terms as revealed by the pre and post lab questions. Additional questions were added after the SS implementation to address

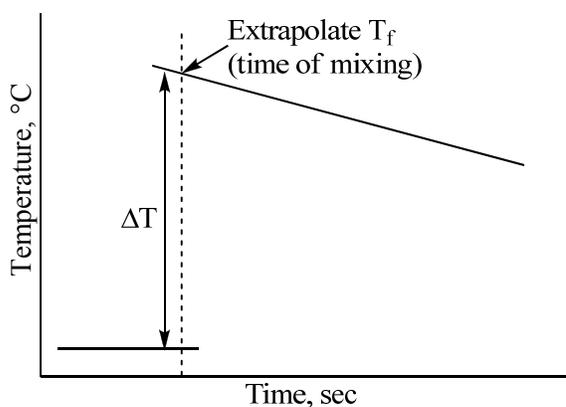
this problem and prompt students to consider the differences in these two concepts (pre-lab question 6 provided in Appendix E). Further analysis with comparison to a control group would be necessary to make additional inferences other than those already explored. Complete rubric, additional data and student responses are provided in Appendix E.

3.5 Thermometric Titration Experiments

Thermometric titrations use the enthalpy change, due to changes in state or heat changes from chemical reactions or interactions, to monitor the progress of the titration and determine the endpoint. Utilizing temperature has been shown to be a simple and accurate method to determine endpoints of typical acid-base and redox titrations (127). Since the thermometric titration measures the enthalpy change at stoichiometric equivalence, enthalpy change (ΔH , J/mol) can be calculated from the thermometric data. However, these experiments are typically performed independently without appropriate instruction to relate these concepts. We have developed a thermometric titration experiment from which students use the data to determine ΔH_n . As a practical benefit this experiment provides a shortened ΔH_n experiment where the enthalpy is derived from the titration data. This experiment demonstrates that chemistry topics are not isolated from each other, but connected and intertwined. In our experiment, each trial of this thermometric titration which took approximately 5-8 minutes per trial experiment compared to the typical calorimetry experiments which are monitored for 15-20 minutes. There are few experiments published which utilize senses (smell and hearing) other than eye sight in making titration determinations (Chapter 1 references 1-4, 6 and 7). Few experiments utilize temperature changes during the titrations to make thermometric determinations of the endpoint (128-132) and are relatively old studies (128,129) or utilize intricate and/or expensive experimental set-up (130,131).

Traditionally, undergraduate acid-base and redox titrations take advantage of colorimetric changes such as using a weak organic acid or base (typically phenolphthalein) (133), permanganate (134,135), or starch-iodine complex (136) and instrumentation such as pH meters (137,138) to determine the endpoint. Computer simulated titrations have been used to allow students to practice carrying out titrations and using sample data (139). These methods have been used in the literature for various studies such as the use of acid-base titrations in non-aqueous solutions (140), determination of pKa values for weak multiprotic acids using pH measurements (141,142), utilization of familiar food products in the laboratory (136,143), and microscale experiments to examine hard water (134).

Traditional ΔH undergraduate experiments produce graphs of temperature vs. time (Graph 3.7), where ΔT is used to obtain heat, q (Equation 3.1) and ΔH (Equation 3.2) by mixing reagents at one time and monitoring the temperature change of the reaction mixture over time (144-147). Other calorimetry experiments add the reagents incrementally to determine ΔT of ratios of reagents to determine ΔH using titration equipment (148) or graduated cylinders (149,150) without making the connection to the use of experiment to titrations and determining the concentration of an analyte.



Graph 3.7. Enthalpimetric graph for the traditional determination of ΔH .

$$q = mc\Delta T = c_t\Delta T$$

Abbreviations:

Equation 3.1. Typical calorimetric equation. c - specific heat capacity of mixture, J/g°C

$$q = -\Delta H(n_p)$$

c_t - total heat capacity of calorimeter, J/K or J/°C

Equation 3.2. Energy and enthalpy equation. q - amount of heat, J

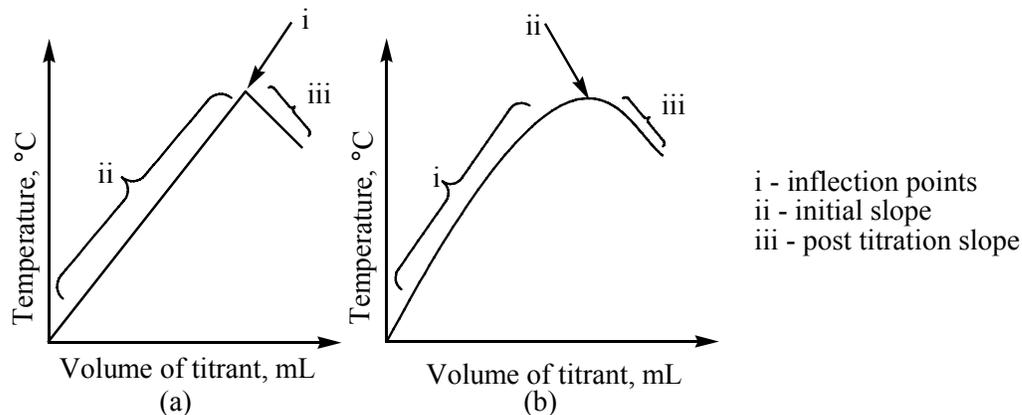
$$\Delta T = -\Delta H_n(M_t V_t / c_t)$$

n_p - moles of product, $M_t V_t$

Equation 3.3. Temperature change equation. m - mass, g

Other researchers have focused on educational assessments (151-153), development of calorimeters (154), or the theory of the experimentation (155). These assessments include studies of how different levels of information presented by various technologies affected students' understanding of acid, base, and pH concepts (151), on students' understanding of acid-base titrations using computer tasks (152), and on whether students have sufficient background knowledge to explain the properties of acids, bases, or salts (153).

In this thermometric titration experiment, the final temperature after each addition of titrant is recorded to obtain data of temperature (T , °C) vs. volume of titrant (V_t , mL). From the data, a graph of T vs. V_t is drawn (thermogram). The thermogram is relatively linear until the end point, after which addition of excess titrant creates an inflection point (127) (Graph 3.8). This inflection point can be used to identify the end point which can be *extrapolated* from the titration graph (T , °C vs. V_t , mL). ΔT is obtained by finding the difference in temperature after each addition of titrant from the *initial temperature* (of analyte) and the graph of ΔT vs. V_t was used to obtain the enthalpy of neutralization (ΔH_n) by the differential Equation 3.4. ΔH_n can therefore be determined from the initial slope, $d\Delta T/dV$, of the ΔT vs. V_t graph (Equations 3.5-3.6). Multi-protic acids yield multiple inflections in the graph such as H_2SO_4 with 2 inflections, one for each ionizable proton (127).



Graph 3.8. Representative thermograms for (a) an ideal titration and (b) actual titration results.

$$d\Delta T/dV_t = -\Delta H_n(M_t/c_t)$$

Equation 3.4. Derivation of calorimetric equations.

$$d\Delta T = \underbrace{-\Delta H_n(M_t/c_t)}_{m\text{- slope}} dV_t + \underbrace{0}_{\text{intercept}}$$

Equation 3.5. Equation for the slope of the thermogram.

$$\therefore \Delta H_n = -mc_t/M_t$$

Equation 3.6. Equation to determine enthalpy.

Abbreviations:

ΔT – $T_f - T_i$ (analyte); K or °C

M_t – molarity of titrant, M

V_t – volume of titrant, L

$d\Delta T/dV_t$ – differentiated equation;

slope, m

Several assumptions were made in order to derive Equations 3.6. Each of these assumptions provides a good opportunity to address various concepts of thermochemistry and titrations with students. Depending on the students' educational stage, each of these assumptions may be directly addressed by the instructor or through investigative questions.

1. The system was assumed to be preventing heat from entering or leaving the reaction mixture and assumes the experiment is adiabatic, at constant pressure (156), therefore the heat capacity of the insulator (covered Styrofoam cups preventing heat exchange), c_a , was assumed to be 0 J/K.

2. Heat capacity of the medium, c_m , was assumed to be the heat capacity of water, which was determined from the product of the specific heat capacity of water ($c_w = 4.180 \text{ J/gK}$) and mass of the aqueous solution (Equation 3.7).

3. Since $c_m \gg c_a$ (127), c_t (total heat capacity of medium and cups) was assumed to be approximately equal to c_m (Equation 3.8-3.10, 156).

$$c_w m_w = c_m \approx c_t$$

Equation 3.7. Approximation of c_t .

$$c_t = c_m + c_a$$

Equation 3.8. Total heat capacity of system.

$$\Delta T = -\Delta H_n (M_t V_t / c_m + c_a)$$

Equation 3.9. Resulting enthalpy equation.

$$\therefore \Delta T = -\Delta H_n (M_t V_t / c_m)$$

Equation 3.10. Enthalpy equation for medium.

c_m was determined experimentally for the medium in the Styrofoam cups (constant-pressure calorimeter) (127,161) using Equation 3.11.

$$q_{\text{cal}} = -q_h - q_c = c_m \Delta T$$

Equation 3.11. Determination of heat capacity of medium.

Abbreviations:

c_m – Heat capacity of the medium, J/K

c_a – Heat capacity of container, J/K

c_w – Specific heat capacity of water

c_t -total heat capacity of system.

Abbreviations:

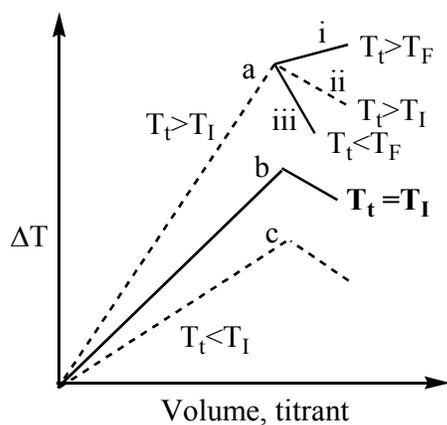
q_h - Heat lost by hot water

q_c - Heat gained by cold water

q_{cal} - Heat of calorimeter (medium + cups).

4. Enthalpy of dilution (ΔH_d) and of solution (ΔH_s) are assumed to be negligible (128,127).

5. Titrant and analyte were at the same temperature, $T_t = T_I$ and the temperature change of the titration represented the internal energy change of the reaction only, $\Delta T = T_I - T_F$ (127, 156). The effect on the initial slope and post reaction slope of the titration curve is affected by the temperature of the titrant (T_t) and the analyte (T_I). Graph 3.9 demonstrates the temperature effects on the initial (a-c) and post reaction slope (ai-iii) slope with reference to $T_t = T_I$ (b) (127). When $T_t > T_I$ (a) the initial slope would be steeper as a result of the higher T_t which raises the overall temperature and when $T_t > T_F$ a more positive post reaction slope (upward- ai) results when compared to titration with $T_t = T_I$ (b).



Graph 3.9. Temperature effect on graph due to the titrant and analyte.

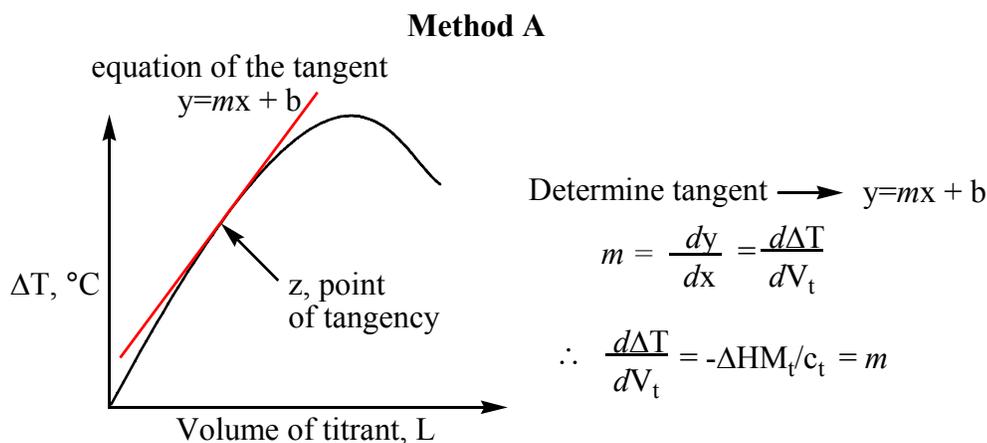
6. Solutions used are pure, with no contaminants. Adding additional reagents may change the shape of the graph as well as change the temperature change observed (127).

7. Titration time is short (127), preventing any dispersion of heat as the Styrofoam cup is not a perfect calorimeter and slowly allows heat transfer to the surrounding.

There are two different methods for determining the initial slope of the curve, obtaining a tangent to the curve or derivation of the curve.

Method A: Tangent to curve (Mathematical Approach)

A tangent line is drawn (Graph 3.10) with any suitable method, such as drawing secant lines in Excel or using a ruler to draw a line of tangency to the curve. The slope of the tangent is determined by calculating the slope (dy/dx) or adding a trend line in Excel to obtain the equation of the line.

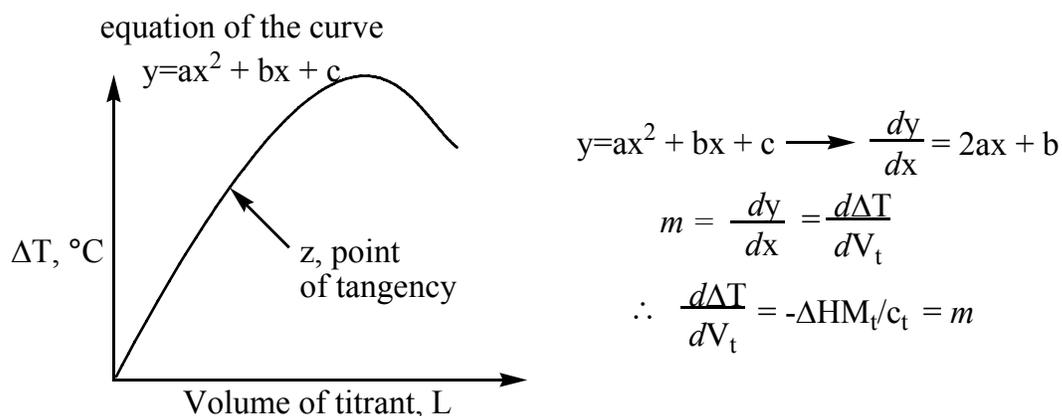


Graph 3.10. Determination of ΔH_n using Method A.

Method B: Alternative trend line method (Excel-Calculus Method)

A polynomial trend line can be obtained using Excel and the equation of the curve (Graph 3.11). The derivation of the polynomial equation allows for the calculation of the slope of the line at point z, point of tangency, using the x coordinate.

Method B



Graph 3.11. Determination of ΔH_n using Method B.

In order to develop this thermometric titration experiment, the chemical considerations included: a) determination of suitable chemicals, b) experimental set-up and procedure, and c) appropriate chemical testing to ensure the thermometric titration data are reliable and accurate. The safety concerns of this experiment are the same as those for traditional titration experiments, therefore general laboratory cautions were taken with the acids, bases and redox reagents.

a) *Suitable chemicals*: Acid-base and redox reagents typically used include NaOH, HCl, HNO₃, AcOH, H₂O₂, MnO₄⁻, KI and Fe²⁺ (128,137,144,146) and these were considered for the thermometric experiment. A sufficiently large negative or positive ΔH was needed to give a large enough ΔT to be easily studied (127). The ΔH_n of a fully dissociated strong acid with a fully dissociated strong base is approximately -56 kJ/mol (-13.5 kcal/mol), which is significant enough to be observed easily with 1 M solutions. A satisfactory endpoint can be obtained for acids with a $K_a = 10^{-10}$, therefore some weak acids are acceptable (127).

Temperature rise is dependent on the concentration of the reagents and almost independent on the volumes used (157). The concentration of the solutions could affect the ΔH_n value obtained (128). Concentrations below $3 \times 10^{-3} \text{ M}$ began to affect the accuracy of the endpoint (158), while

increased concentrations give greater ΔT and increased ΔH_d (157,159) creating misleading results. ΔH_d was assumed to be negligible at low concentrations, however more concentrated reagents produce sharper titration curves. The common concentration of acid and base used in titrations is 1 M with volumes of 10-25 mL of the reagents, while 0.02-0.2 M redox reagents at a volume of 10-20 mL are used. Typical ΔH_n experiments use 1-2 M solutions with 50 mL volumes of the acid and base (149). The dimensions of the cups dictated the depth of the analyte in the cup and therefore appropriate minimum analyte volume (10 mL) necessary to ensure the thermometer had appropriate contact with the solution without touching the bottom and sides of the cup. The Styrofoam cups used held a total volume of 250 mL with the dimensions of 7.8 cm (top diameter), 4.5 cm (bottom diameter) and 8.8 cm (height). Concentrations of 1.0 – 2.0 M acid/base solutions (also shown in the ΔH_n determination) and 0.03 and 0.20 M for the reducing and oxidizing agents respectively were determined by experimentation for the most reliable minimum concentrations.

b) *Set-up and procedure*: Pipets and burets were used to provide exposure to titration glassware commonly used in laboratory courses (psychomotor information) and to generate accurate results. Incremental addition and continuous addition are two methods used to study ΔH_n . Incremental addition is more accurate as it gives time for temperature equilibration (127) and is accomplished with the use of the pipet and buret. Improving the heat capacity of the apparatus improves the graph obtained (127). Dewars are excellent insulators; however, they take a lot of time for temperature equilibration. Styrofoam cups are not perfect insulators, but for this experiment they provide reasonable data. The reaction mixture needs continuous stirring to allow for even distribution of reactant. Stir bars are placed in the Styrofoam cups and placed on stir plates (Figure 3.19). Accuracy and response of temperature recording instruments (thermometers, thermocouples and thermistors) have an effect on titration results as they should record the temperature in a relatively short period of time (30 seconds) and to at least 0.1°C. Curvature at the endpoint may also

be due to insensitivity of instruments (127). Digital, alcohol thermometers and thermistors were evaluated. The digital thermometer and thermistor fulfill both criteria and are available in most teaching laboratories.

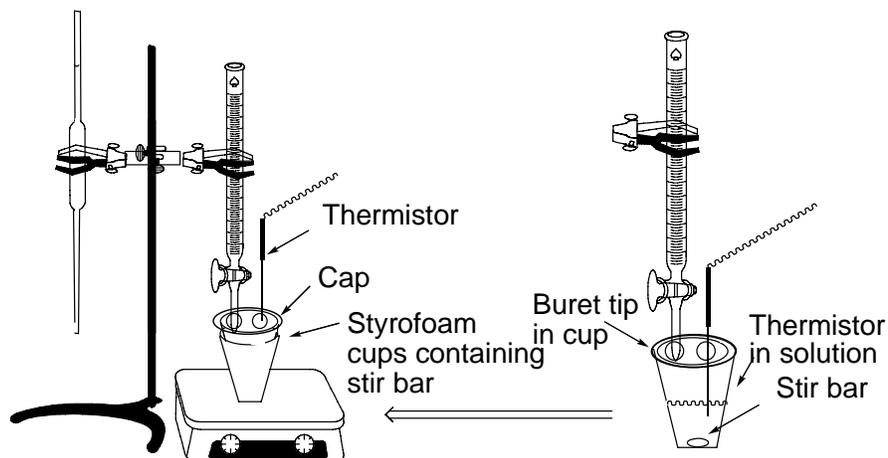


Figure 3.9. Thermometric titration apparatus.

Other factors that could affect the titration are the solvent, temperature of the reagents and reaction or addition times. Water was used as the solvent as all reagents used were primarily water soluble; therefore ΔH_s is not an issue (160). Reagents were allowed to equilibrate to the same temperature by allowing the solutions to sit at room temperature at least overnight (Graph 3.9). A cover (weigh boat or plastic lids) was used not only to reduce heat transfer to the surroundings but also to prevent the students from using any visual changes to make determinations. Two small holes in the cover were made to allow the thermometer to be placed in the mixture and the tip of the buret to deliver the titrant (Figure 3.19).

c) *Testing*: The titration method, reagents and ΔH_n calculations were tested and compared against traditional methods. Table 3.26 shows endpoint volumes extrapolated from the thermogram (titration graph) and calculated molarity values for the thermometric and colorimetric titrations of various acids using 10.0mL standardized 0.959 M NaOH solution. Any of these acids would be good candidates for the titration. HCl and HNO₃ (strong, monoprotic) were selected for the experiment.

Table 3.26. Comparison of colorimetric and thermometric titration data using 10.0 mL NaOH.

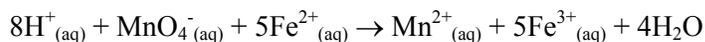
Acid	Thermometric		Phenolphthalein	
	Acid Volume, mL	Molarity, M	Acid Volume, mL	Molarity, M
HCl	9.80±0.05, n=10	0.979±0.00	9.87±0.02, n=3	0.972±0.03
H ₂ SO ₄	10.90±0.02, n=7	0.440±0.02	10.90±0.10, n=3	0.440±0.004
HNO ₃	10.10±0.06, n=8	0.950±0.01	10.05±0.07, n=2	0.954±0.07
Acetic	9.80±0.07, n=6	0.979±0.01	10.00±0.10, n=3	0.959±0.01

Additional testing was performed by two undergraduate student volunteers. The first student volunteer's (FV) data showed that a student previously unfamiliar with the thermometric titration technique can reproduce with accuracy and precision the titration data (Table 3.27). The calculated concentration for the data obtained by the second volunteer (SV) of 0.96 M HCl titrations was 0.93 ±0.02 M, n=4.

Table 3.27. Thermometric titration data obtained from the first student volunteer for four acids.

Acid	Calculated Molarity, M	Actual Molarity, M
HCl	0.95±0.01, n=4	0.97
H ₂ SO ₄	1.00±0.05, n=4	0.44
HNO ₃	0.98±0.03, n=3	0.95
AcOH	0.96±0.05, n=3	1.01
Used 0.959 M standardized NaOH for HCl, H ₂ SO ₄ and HNO ₃ ; 1.029 M for Acetic.		

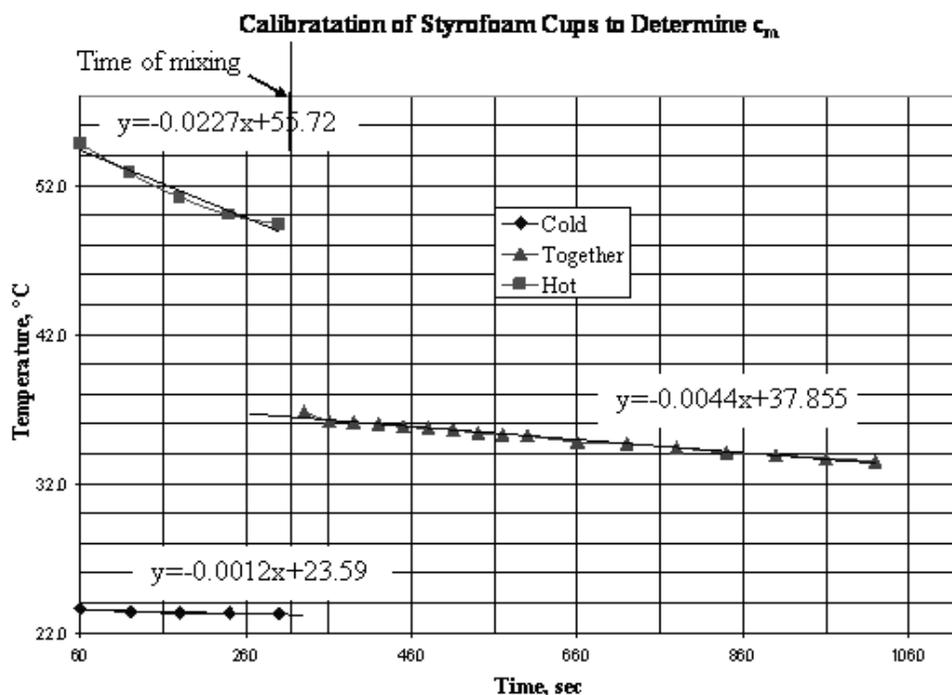
Similar observations were obtained for the redox reactions and therefore thermometric titrations employing the heat change of a redox reaction was also incorporated. For the redox titration of MnO₄⁻ with Fe²⁺, an intrinsic colorimetric change is obtained.



In the redox titration using standardized 0.025 M KMnO₄ as the oxidant, the visual and thermometric titrations gave the same endpoint volumes of the titrant resulting in a calculated concentration of the analyte as 0.166±0.006 M Fe(NH₄)₂(SO₄)₂·6H₂O (Fe²⁺) n=3. Other redox systems were explored including using Ce³⁺ as the reducing agent and Cr₂O₇²⁻ as the oxidizing agent, however, Fe²⁺ and MnO₄⁻ performed best and reliably, therefore were used in our sensorial experiment. An opaque

weigh boat was used as the cover on the titration vessel preventing students from seeing the color change.

The c_m value was determined experimentally using Equation 3.11, where c_m was assumed to be c_t (Equation 3.6). The experimental data for the equal volumes of warm and cool water before and after mixing were plotted to produce Graph 3.12, where the lines were extrapolated to find the ΔT between the mixture and hot and cool water (Equation 3.11). The average values of c_m for a total 40-100 mL of water are shown in Table 3.28.



Graph 3.12. Graph of temperature vs. time for calibration of the Styrofoam cups to determine c_m .

Table 3.28. The experimental and calculated values for the heat capacity of the medium (c_m).

Volume of total water, mL	Experimental c_m , J/K	Calculated c_m , J/K
40	$158.7 \pm 1.9, n=4$	167.2
50	$202 \pm 22, n=2^*$	209
100	$399.4 \pm 9.36, n= 4$	418
* SV data: Water was not weighed, but measured in graduated cylinder.		

The value for c_m was also approximated from Equation 3.10, which was a simple, non-experimental method that students can use to estimate the c_t based on their titration data. At relatively low concentrations of acid and base, the density of the solution can be assumed to be that of water (1.00 g/mL) to obtain an approximation of the reaction's mass at the endpoint (Table 3.28). The calculated values were comparable to the experimental; however, the calorimeter was not a perfect insulator and introduced difference in the values (~ 10 J/K less for each). The actual c_m values would also be different from those calculated due to slightly lower heat capacities and the slightly larger densities of dilute HCl, NaOH and NaCl solutions than that of water (Table 3.29) (161). Since each solution possesses different values complicating the calculation, water provides a good estimation of c_m and was used for the ΔH_n calculations.

Table 3.29. Density (dependent on the concentration) for $\sim 0.5 - 1.6$ M HCl, NaOH, NaCl.

Density, g/mL			Actual Concentration, M		
HCl	NaOH	NaCl	HCl	NaOH	NaCl
1.0081	1.0196	1.0207	0.553	0.523	0.510
1.0179	1.0413	1.0318	1.117	1.069	1.043
1.0278	1.0648	1.0633	1.691	1.597	1.637

Our thermometric titration data were compared to the traditional method for determining ΔH_n . The data were plotted as temperature vs. time on a graph similar to Graph 3.7 and each line was extrapolated to the time of mixing to find ΔT (Equations 3.1 and 3.2). The results of the traditional method and the calculations from the thermometric titration are summarized in Table 3.30.

Table 3.30. ΔH_n data for traditional and thermometric titration experiments at various concentrations.

Concentration, M	ΔH_n , kJ/mol	
	Traditional Method	Thermometric titration ($c_m = 167.2\text{J/K}$)
5.44±0.56, n=3	-60.62±0.23, n=3	-64.65, ±1.84, n=3
3.16±0.02, n=3	-54.71±1.19, n=3	-58.57±0.24, n=3
2.12±0.01, n=4	-53.84±0.94, n=4	-53.68±2.42, n=4
1.03±0.00, n=3	-54.16±1.12, n=3	-54.06±0.59, n=3
0.511±0.009, n=3	-51.59±2.71, n=3	-55.06±2.31, n=3
0.237±0.005, n=3	-48.50±3.41, n=3	-52.94, ±3.53, n=3
Literature value: -55.7 to -57.3 kJ/mol; varies depending on determination method (157,162).		

The effect of concentration was explored using concentrations from 0.227-5.44 M acid. The ΔH_n range for acids and bases at concentrations of 1 -2 M was comparable to the literature range. The fluctuations in the data may be a result of varying quantities of heat lost over time (hence importance of short time), temperature of the calorimeter before starting the titration (did not equilibrate), very low concentrations affecting accuracy, or changes in ambient temperature for experiments performed at different times or days causing the temperature to fluctuate significantly. Concentrations higher than 2 M, in general, appeared to give higher ΔH_n values, which may be a result of increased ΔH_d (Table 3.31) (163).

Table 3.31. ΔH_d values at infinite dilution for various concentrations of HCl.

Molality, mol/kg	ΔH_d (HCl), kJ/mol
0.2	-0.761
0.5	-1.172
1	-1.695
2	-2.623
6	-6.268

The second volunteer's traditional and thermometric data was compared for 1 M HCl where ΔH_n was calculated as -55.3 ± 1.6 kJ/mol, n= 3 and -57.9 kJ/mol, n=1 respectively. The ΔH_n for various acids were calculated and compared to FV's data (Table 3.32). The calculated ΔH_n for strong acids were comparable to the literature ΔH_n value; however, AcOH was slightly lower, due to being

a weak acid (approximately -53 kJ/mol) (149,164). The ΔH_n calculations for HCl and HNO₃ at 1 M were considered reasonable for the experiment and chosen to be used in the teaching lab.

Table 3.32. Comparison of data for various ~ 1M acids.

Acid (~1 M)	Calculated ΔH_n , kJ/mol		
	Researcher	FV	SV
HCl	-54.16±1.12, n=3	-56.49±1.76, n=4	-57.9, n=1*
H ₂ SO ₄	-51.66±3.71, n=2	-58.350±2.67, n=3	
HNO ₃	-54.82±4.62, n=3	-52.09±2.41, n=3	
AcOH	-50.40±0.78, n=2	-48.21±3.17, n=3	

* Only one trial was performed other than the rough trial.

Thermometric titration LLR objectives and associated mental operations

The pedagogical objectives of the thermometric experiment and the assessment of these objectives were aligned with the structure of the LLR and developed using the M&K framework (Table 3.33). The systems and mental operations necessary for these objectives demonstrate the cognitive skills required, where the lower cognitive levels are also necessary to achieve these objectives (hierarchical nature M&K).

Table 3.33. Titration LLR pedagogical objectives and assessments.

Objectives:	Assessed/observed by:	Mental operations:
Students will explore enthalpy changes of dissolution and dilution reactions by investigating heat transfer and temperature changes. <i>Systems:</i> Comprehension	a) Construct symbolic representation of the reactions at the microscopic level to explain physical manifestations of heat. b) Explanation of tactile observations in relationship to temperature change. c) Connect observations to the use of Styrofoam for coffee cups.	Symbolizing and integrating
Students will observe a demonstration of a colorimetric titration to observe the titration procedure to gain knowledge of proper technique. <i>Systems:</i> Comprehension and analysis.	a) Make comparisons between colorimetric and thermometric methods. b) Process and be able to explain psychomotor information. c) Explain reaction at the microscopic level during the addition of the titrant.	Matching, specifying and integrating.

Table 3.33. Titration LLR pedagogical objectives and assessments (continued).

Objectives:	Assessed/observed by:	Mental operations:
Students will conduct thermometric titrations, effectively monitoring titration and their performance to investigate thermal observations. Systems: Metacognition and comprehension.	a) Perform titration successfully using psychomotor information gained. b) Decide number of data points need to effectively obtain accurate data. c) Determine how changes in the order of addition or reagents affect titration.	Specifying goals, monitoring processes, analyzing errors, and integrating.
Students will explore stoichiometry and titration calculations using the data. Systems: Comprehension and knowledge utilization	a) Write and balance equations, including using the standard reduction table to deduce the redox equation. b) Calculate unknown concentration.	Symbolizing and solving problems
Students will use and manipulate the titration and correlate thermodynamics and solution chemistry. Systems: knowledge utilization comprehension	a) Describe or make connection between the thermometric titration and pre-lab activity. b) Identify endpoint using the graph. c) Calculate the ΔH_n .	Integrating, making decisions and solving problems.
Students will demonstrate understanding and draw conclusions. Systems: Comprehension, knowledge utilization, analysis and metacognition.	a) Extension of knowledge by proposing questions and reasonable answers. b) Make conclusions on enthalpy changes and how it was observed. c) Depict titration pictorially.	Integrating, symbolizing, monitoring clarity and process, matching, specifying
Students will solve problems (pictorial and algorithmic) that promote critical thinking Systems: Knowledge utilization, comprehension, analysis.	a) Identify weak and strong acids, bases and conjugate pairs. b) Solve algorithmic problems and calculate ΔH_n using data.	Matching, solving problems, analyzing errors, symbolizing.
Students will self-reflect and examine self-efficacy. Systems: Self-system thinking and metacognition.	a) Rationalize results to identify the importance of the concepts. b) Suggest improvements to the experimentation c) Revise pre-lab responses. d) Utilize learning aids provided.	Examining importance, efficacy, monitoring accuracy and process.

Misconceptions, Interventions and Conceptual Question Development

The following are misconceptions and developed interventions that specifically address problems with acid-base & redox chemistry and ΔH_n /thermodynamics with corresponding calculations. The summary includes: a) misconceptions found in the literature, b) the most relevant interventions and suggestions, c) developed interventions to specifically address these misconceptions, and d) conceptual questions to evaluate these misconceptions. After the experiment was implemented, the experimental procedure and conceptual questions were modified in response to identified learning difficulties observed during the experiment. An intervention pre-lab activity was performed prior to the second implementation of this experiment.

1. Acid-base properties and neutralization: The extent of a neutralization reaction in relation to the strengths of acids and bases is often misunderstood (*152,166,*), possibly as a result of misunderstandings of weak acids and bases as well as the resulting conjugate pairs (*166,167*). The type of interaction (chemical or physical) associated with the reaction is commonly misunderstood by students, where acids are thought to be broken down or ‘changed from acids’ when neutralized (*152,168*). Neutralization is frequently thought of as just a mixing of the acid and base or the dominance of the acid over the base (physical interaction), rather than a chemical reaction. The inability to correlate acid-base reactions and thermodynamic principles results in the failure to recognize and understand the enthalpy change (*170*). Research has shown that: a) students are less likely to identify a base, b) believe that pH only relates to acids, c) see acids as the reactive species, or d) demonstrate that acids are stronger or more powerful than bases (*152,168,171*). Furthermore, the strengths of acids and bases are often correlated to molarity, rather than to the ability to transfer or accept a proton (*171,172*). Students may believe that conjugate pairs consist of only positively and negatively charged ions, which will neutralize each other (*166*), which is again related to the misconception on strength (*162*). Bradley and Mosimege have found that ‘diprotic’ may be confused

with ‘amphoteric’ (173). A misconception observed from our first implementation involved students equating equilibrium with the endpoint of strong acid-base and redox reactions. This misconception may be a result of their misunderstanding of the strength of the acids and bases.

Literature Interventions and suggestions

- a) Schmidt suggests using a newer definition of neutral as an aqueous solution where H^+ and OH^- concentrations are both $1.0 \times 10^{-7} M$, rather than “two substances that consume each other”, as the scientific language used in everyday situations may create misconceptions (162). This problem is also been discussed by Nakhleh as a result of the cognitive-model of learning (169).
- b) Nakhleh suggest that pictorial representations aid students’ understanding of the macroscopic and microscopic levels as students construct their own definitions (169). Smith and Metz suggest the use of diagrams in explanations rather than relying heavily on mathematical problems as pictorial questions on microscopic representation can evaluate students’ understanding of the concepts (124).
- c) Taber used pictorial representations of concentrated and dilute solutions of a strong and weak acid to probe students’ ability to distinguish acid strength and concentration (Figure 3.10) (101).

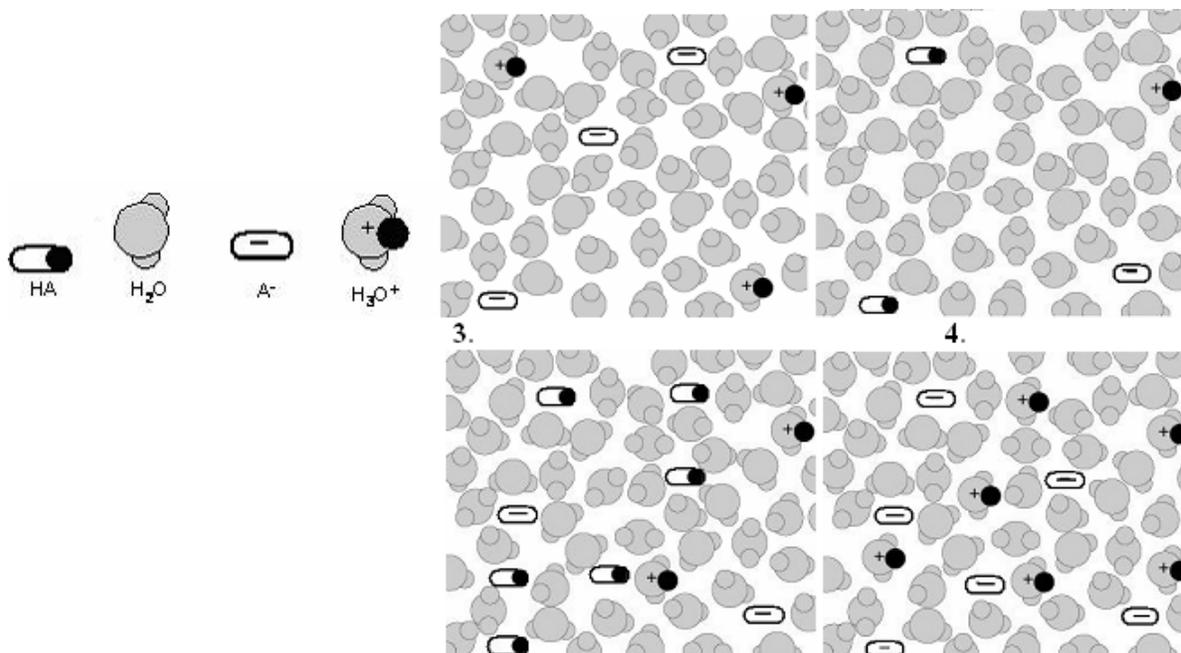


Figure 3.10. Taber's diagram depicting an acid at different concentrations and strengths.

d) Concept maps have been used as evaluation tools (101,171). Ross and Munby state that the challenge for instructors is to aid students to construct 'networks of meanings' that are in agreement with accepted chemical theory as everyday concepts tend to persist after instruction (171).

e) Nakhleh and Krajcik suggest that different levels of information from various methods (colorimetric titration, pH meter, and microcomputer-based titrations) affect students understanding of acid-base and pH concepts. Their research suggests that more advanced technology (microcomputer-based laboratories) allow students to focus on their observations and allowed reflection on the phenomena under investigation (137), rather than focus on the methods.

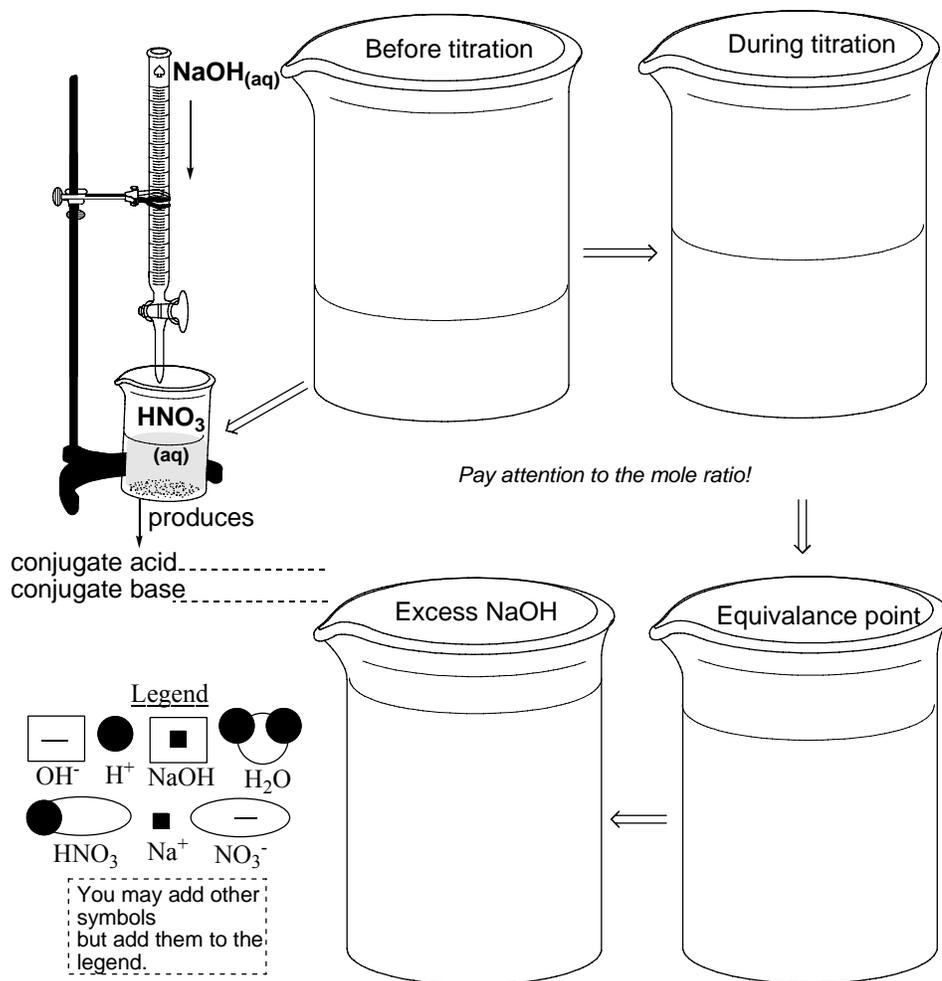
f) Calton provides a method to teach acid-base chemistry without involving equilibrium. The author suggests that the complexities of equilibrium can be avoided by treating the reactions as all-or-none and also providing students with a table of acids in order of strength. (192).

Developed Interventions and Concept Testing

i) The terminology used to describe neutralization relied on the concentrations of H^+ and OH^- , and was reinforced during both the demonstration of a colorimetric titration and the sensorial experiment. The conceptual questions were phrased to incorporate the reaction of H^+ and OH^- as the neutralization reaction (post-lab question 1).

ii) Rather than remove the manipulation of the titration equipment shielding students from the titration methods, students used pictorial representations of the acid-base reaction in the pre and post-lab questions to encourage a closer look at the molecular level. The acid strength and concentration were examined in the pre-lab with a pictorial question adapted from Taber (Figure 3.10) by connecting the molecular observations to the terminology (matching and integrating skills). The diagram of acid strength aided the rationalization of the extent of the dissolution of the acids and prevents the idea that equilibrium is equivalent to end-point. Post-lab question 1 requires students to demonstrate the species present at various stages of the titration. Just as with the ASA kinetics experiment, students were not specifically instructed in the lecture portion of the course on the particulate nature of matter. The questions therefore evaluated students' understanding at the microscopic, macroscopic and symbolic representative levels as it related to the experiment.

Post-lab Question 1: Complete the diagram below to depict the interaction of the reacting species in Part B that led to neutralization. Referring to the diagram, explain why the highest temperature is used as the end point.



iii) Students were asked to correlate temperature data to ΔH_n and compare thermometric titrations with the colorimetric titration. The data was also used to make connections between the acid-base reaction and molecules' properties in the titration solution (Pre- and Post lab question 1).

2. Redox reagents and reactions: The reagents that constitute oxidants or reductants may not easily be identified or understood. Nakhleh suggests that this problem may be exacerbated by the differing definitions in different courses as redox has been described as a change in oxidation number (oxidation number) and loss or gain of oxygen or electrons (7). Oxidation number is often seen as synonymous with valence, formal charge and coordination number (175), causing students' difficulty in determining oxidation numbers. However, providing students with oxidation numbers rather than

learning its determination can lead to misconceptions (172). Students may believe they can track the flow of electrons by the change in charge of the species (162,172) and monatomic and polyatomic ions charges are often confused with oxidation number (174). Students may incorrectly identify the reduction and oxidation reactions taking place and not able identify the changes taking place (174). Students sometimes believe that oxidation and reduction occur independently.

Literature Interventions and Suggestions

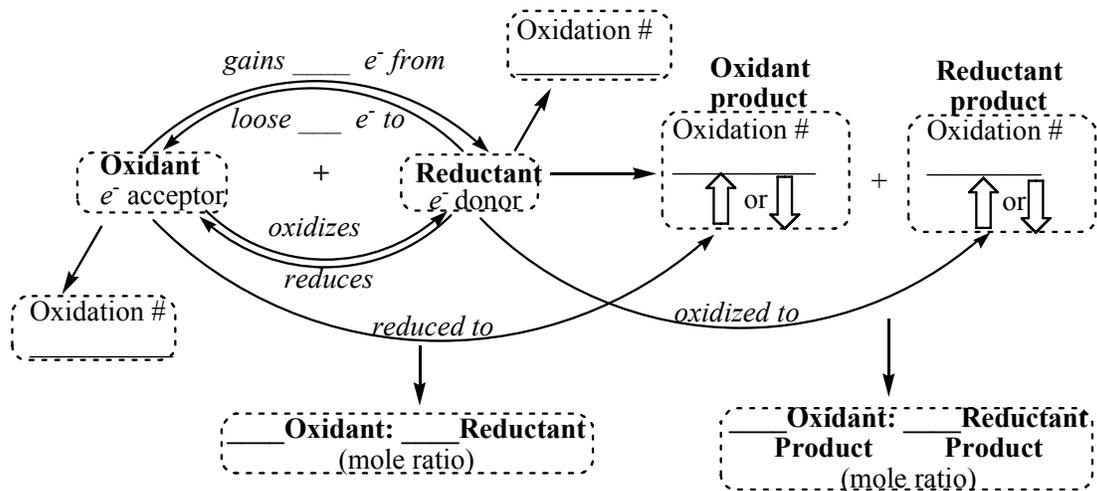
- a) De Jong et al. suggest that there is an overemphasis on the importance of algorithms which creates problems, so students should be encouraged to develop their own methods of problem solving. Listening to, observing students as well as encouraging collaborative work can facilitate clarification of concepts (174).
- b) Garnett and Treagust suggest using one definition of oxidation-reduction, as multiple models for the same scientific behavior leads to confusion, where they suggest that redox reactions and reagents can only be successfully identified with certainty by oxidation numbers (174).
- c) Contrary to Garnett and Treagust, De Jong et al. suggest omitting oxidation numbers as much as possible, but rather provide students with a set of rules for identifying redox reactions including clear definitions of redox using electron transfer (172,174).
- d) Herron suggests that the word association between oxidation-reduction and oxidation number is stronger and more logical for students (176). Cox and Cox suggest that the use of electron transfer is inconsistent with basic arithmetic, which is therefore not intuitive to students and causes confusion (177). However, many textbooks incorporate the use of electron transfer with (178) or without the use of oxidation numbers (179).
- e) Parkin and Smith have defined, set clear rules for determining oxidation numbers and provided examples of when valence, formal charge and coordinate numbers will differ (175).

Developed Interventions and Testing

i) The definition of redox chosen utilized the change in oxidation numbers and the resulting electrons transferred to determine the reductant and oxidant. Post-lab question 2 connects each factor (oxidation number, electron transfer and mole ratio) and students are referred to this diagram when writing the redox equation used in the experiment. Each factor individually appears to create misconceptions or is disputed as to its effectiveness in the literature; however making connections between them may clarify problems.

Post-lab Question 2: Using the reaction in Part C, replace the bolded words in the diagram with the reactants and products in the experiment by filling in the blanks below the diagram.

- ii) Calculate and fill in the oxidation numbers of the reactants and products in the diagram.
- iii) Circle the arrows indicating if the oxidation number increased or decreased.
- iv) Give the stoichiometric ratios between the reactants and the ratio between the products.



Oxidant

Oxidant product

Reductant

Reductant product

This diagram requires students to: a) focus on each definition, b) relate the definition to the reagents used in their experiment and c) reflect on the connection between the definitions.

3. Thermodynamic concepts: Concepts of heat transfer, temperature change, enthalpy change and related terminology present several misconceptions. Heat is sometimes interpreted to be a substance that can be added or removed from an object or reaction, instead of the transfer of thermal energy as a result of temperature difference (180,181). Students have a tendency to perceive temperature as synonymous to heat, rather than a measure of the average thermal (kinetic) energy per molecule indicating a change in heat (150,181-185). Symbols used, such as Δ , may lead to confusion (186) and students may not recognize the relationship between heat flow, specific heat, and temperature change (182). This is possibly due to students clinging to the layman definition of heat rather than adapting chemical terminology (7). Enthalpy is often considered as a measure of the heat of a system or heat capacity of the system, rather than the difference in heat from the products to the reactants at constant pressure (overall heat absorbed or released from a system) (180,185).

Literature Interventions and Suggestions

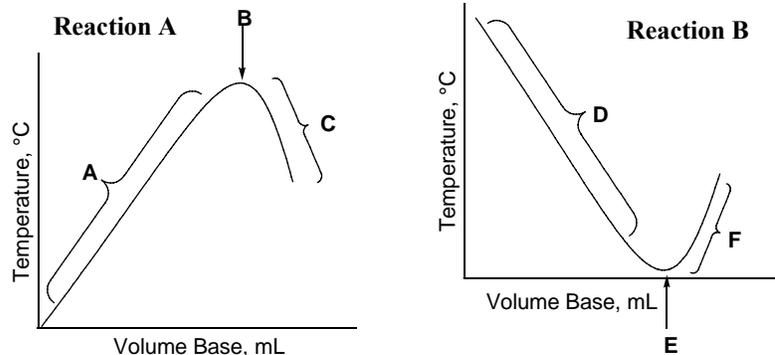
- a) Beall poses three in-lab writing questions for students regarding thermodynamics (temperature of a released compressed gas, definition and use of enthalpy and Gibb's free energy calculation) to observe their misconceptions. The writings of good students were shown to the class to clarify difficult topics (185).
- b) de Vos and Verdonk developed an experiment in which students could observe in temperature (direct experience) in order for them to make connections between temperature and chemical reactions. The students are given questions to guide discussions on their observations and indirectly exposed them to acid-base concepts (150).
- c) Niaz suggests that thermochemistry and kinetic-molecular theory aid students' ideas on temperature and heat, however, students will sometimes hold on to their own beliefs (185).
- d) Barrow suggests removing the "slippery" terms heat and work and replacing them with energy or using the terms in an active manner such as "doing work" or "heating" (183).

Developed Interventions and Testing

- i) Students explored by touch endothermic and exothermic reactions in a brief inquiry pre-lab activity preceding the titrations as part of the second implementation. Students related energy changes using enthalpy diagrams in the pre- and post laboratory questions. Students monitored the temperature changes and relate the change to their sensorial observations. The terminology of the activity, subsequent questions and the post-lab questions involved the use of energy change, heat transfer, enthalpy change and temperature change to specifically make connections between these terms. Students were asked to describe energy and temperature changes in terms of heat transfer (active use) and enthalpy change.
- ii) Students drew (pre-lab activity question 1) or utilized (post-lab question 3) diagrams to explore enthalpy at the molecular level or through graphs rather than just relating definitions. Activity and post-lab questions were used to probe students understanding of the concepts, as well as allow students to think more critically about the concept. Students drew diagrams and used graphs depicting exothermic and endothermic titrations to explain the enthalpy, temperature and reaction changes.

Activity Question 1: Depict microscopically the chemicals before and after the reaction for the assigned reaction.

Post-lab Question 3: The graphs below represent two different acid-base thermometric titrations. Indicate what is occurring in the reaction flask at the parts labeled A-F in terms of the acid and base reacted, temperature and energy changes during the titrations.



iii) Students were encouraged to discuss concepts with other students and the instructor during the demonstration. The short activity preceding the titrations allowed for the misconceptions to be addressed, as well as motivate students to consider the concepts at a higher level.

4. Stoichiometry and solution chemistry calculations: The stoichiometry of both acid-base and redox reactions frequently pose a problem for students. Improper application of mole concepts, “quantity=concentration” of a substance, and “limiting reagent = lowest stoichiometry” are areas in which this misconception is displayed (137,186,187). The function of a standard solution and related calculations is often misunderstood, particularly when the stoichiometry is also not understood. Students often hold misconceptions about what constitutes a solution (solutes in a solvent) and the resulting molarity in terms of the composition of the solution (molecules/ions present and their qualities, etc.) (186).

Literature Interventions and Suggestions

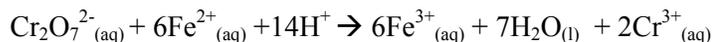
a) Frazer and Servant have shown that students who can do the correct titration calculations without the use of a simple equations such as $M_1V_1=M_2V_2$ often understood the stoichiometry involved in the titrations. Various approaches to volumetric analysis calculations may be done to aid students when using stoichiometry, however the commonly used $M_1V_1=M_2V_2$ method may be a ‘suitable crutch’ for weaker students but does not evaluate the misunderstandings about the reaction at the microscopic level (188).

b) De Jong et al. suggest instructors should allow students to develop their own method for balancing redox reactions (172), while some references provide steps which can be used in a titration for balancing reactions and calculating molarity (189).

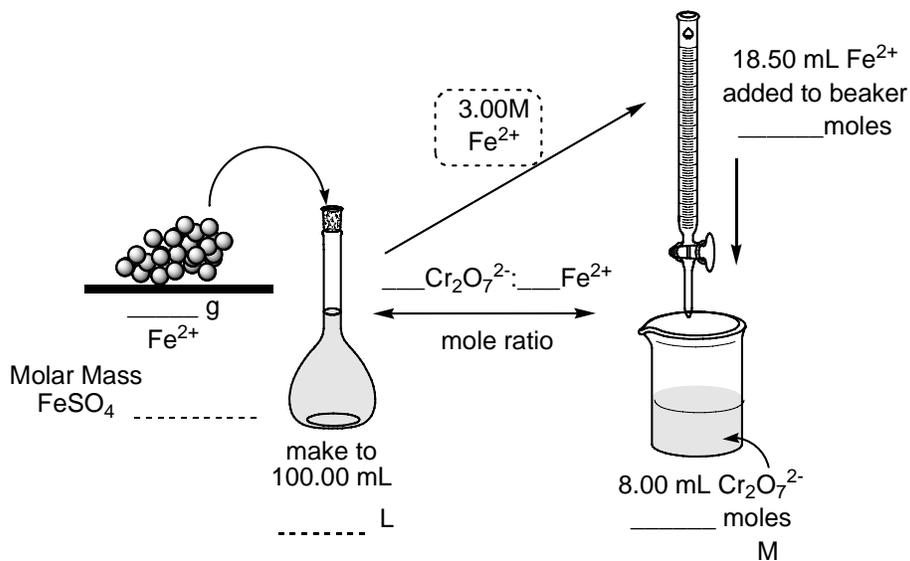
Developed Interventions and Testing

i) Pictorial pre-laboratory questions demonstrated each step of the calculations to prompt students to consider the reaction at the microscopic level, promote a sequential calculation method and observe each of the students' steps in solving the problem (pre-lab question 2). Students represent an acid-base titration and the related calculations with a diagram similar to that in pre-lab question 2 (pre-lab question 3).

Pre-lab Question 2: You make a 3.0 M solution of iron II sulfate. You determine the concentration of potassium dichromate that completely oxidizes the iron II sulfate solution using the reaction as shown below.



Complete the diagram below to determine the concentration of dichromate and show all calculations.



Pre-lab Question 3: Draw a diagram like question 2 depicting the thermometric titration data given. Calculate the concentration of NH_4Cl and c_t . Is the reaction exothermic or endothermic? Show all calculations!

ii) Students were given a calculation diagram which relates stoichiometric principles to their calculations (Figure 3.11). Students were asked also to develop their own generic calculation algorithms in the Results and Discussion section of the LLR.

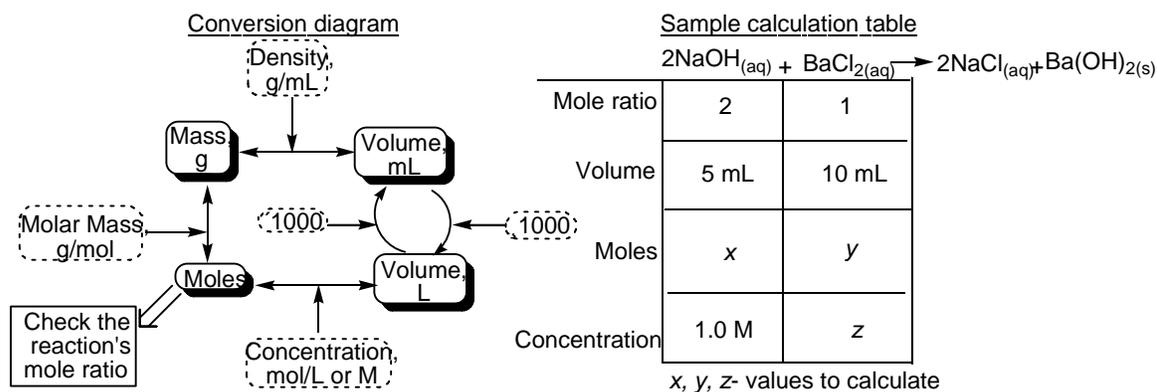


Figure 3.11. Calculation and conversion diagram.

5. Symbolic representation: The emphasis on algorithms rather than a conceptual understanding may create misconceptions (124). Inability to visualize solutions or reactions at the molecular level and symbolic representations of the reagents probably affect students' perception of titrations (188), particularly the belief that titration is a process where one reagent outnumbers the other with no chemical interaction (152). Students who are unable to understand the reaction at the particulate, macroscopic and symbolic representative levels may experience problems understanding the purpose of the titration and explaining reactions explored.

Literature Interventions and Suggestions

a) Nakhleh suggests that students should be reminded that if they can't explain a concept in molecular terms, then they really don't understand it (7).

b) Small groups are suggested to promote higher-order cognition among students, display or discuss their conceptions leading to a better understanding (191) encourage and motivate students (166), or provide a format for misconceptions to be identified and addressed (65,166).

Developed Interventions and Testing

i) Students were asked to depict pictorially the reactions at the molecular and macroscopic levels, relating them to the thermometric titration starting from the pre-lab activity through the post lab questions. These questions prompted students to think critically about their conceptions, to promote an understanding of the reactions at the molecular level.

ii) Students performed this experiment in groups of 2-3 students in an inquiry format to allow students to discuss among themselves the concepts. Students were encouraged to make observations and collaboratively draw conclusions.

Pre-lab intervention activity

The pre-lab intervention activity (discussed in the pedagogical section) was developed to explore heat transfer through glass and Styrofoam (insulator) to observe the ΔT of exothermic and endothermic reactions (150). The activity was developed after the first implementation to aid students misconceptions on thermometric concepts and reinforce correct terminology. This short activity was performed prior to the experiment, therefore the chemicals used needed to be relatively hazard-free and observations easily perceived in a short time. The observations were performed using touch and a digital thermometer to record changes in temperature between the reaction temperature and the ambient temperature. Various endothermic and exothermic reactions that would produce significant changes in enthalpy were explored, which included dilution of an acid and dissolution of hydroxides, ammonium salts, and KCl. These reactions were evaluated to determine necessary volumes and concentrations of reagents.

The endothermic dissolution of NH_4^+ salts and exothermic dilution of H_2SO_4 were chosen as they produced reasonable tactile observations. The dilution of 0.5g of KOH in 5 mL also provided a reasonable exothermic change that was easily observed by touch (Table 3.34). These reactions were observed in test tubes and Styrofoam cups and the corresponding temperature changes were recorded. The differences in intensity of the observations are a result of the concentrations used ΔH_d and ΔH_s , where excess salts were dissolved and 6 M H_2SO_4 was diluted as a safety measure. The reactions chosen allowed for the observation of warm or cold solutions through the test tube, corresponding the increase or decrease in temperature. However, students observed that even through these observations were barely noticeable through the Styrofoam cups, the temperature increase or decrease of the solution as measured by the thermometer remained the same. Additional results, including data for different concentrations, are given in Appendix F.

Table 3.34. Observations by touch through test tubes and Styrofoam and temperature changes.

Reaction	Observation by touch		Temperature Change, °C	
	Test tube	Styrofoam cups	Test tube	Styrofoam cups
$\text{KOH}_{(s)} + \text{H}_2\text{O}_{(l)}$	Very warm	Slightly warm, barely noticeable	29 to 35	30 to 35
$\text{H}_2\text{SO}_{4(aq)} + \text{H}_2\text{O}_{(l)}$	warm	Slightly warm, barely noticeable	28 to 35	30 to 35
$\text{NH}_4\text{Cl}_{(s)} + \text{H}_2\text{O}_{(l)}$	Very cold	Slightly cool, barely noticeable	28 to 20	30 to 20
$\text{KOH}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{KOH}_{(aq)}$ - Dissolved ~0.5g KOH in 5mL of water. $\text{H}_2\text{SO}_{4(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{4(aq)}$ - Diluted 5mL of H_2SO_4 in 2mL of water. $\text{NH}_4\text{Cl}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{NH}_4\text{Cl}_{(aq)}$ - Dissolved ~0.5g NH_4Cl in 5mL of water.				

Implementation Results and Conclusions

This titration experiment was first performed by 32 first semester (FS) general chemistry students in two concurrent sections. After the experiment, the procedure and questions were modified to address problems observed during the first implementation. The experiment was again performed by 20 second semester (SS) general chemistry students in 3 sections. In addition, the SS were asked to calculate the ΔH_n for the titration of HCl with NaOH. Both FS and SS students had the same professor for the lecture section of the course, but different teaching assistants. Similar to the ASA hydrolysis, the researcher served as an observer and provided instruction to the teaching assistants in the FS implementation, but was the instructor for the SS implementation.

The SS students performed the intervention activity prior to performing the titrations. Students made visual and tactile observations for one of three reactions: exothermic dissolution reaction of KOH, endothermic dissolution reaction of NH_4Cl and the exothermic dilution of sulfuric acid. Students collected data on the other reactions from other groups in the laboratory. The criteria for evaluating students' pre-lab activity results were based on the degree of correctness and completeness of the question. A rubric based on the correctness was used to classify the students' response (Table 3.35): correct and complete (C &C), correct but not complete (C), partially correct but incomplete (SC) and, neither correct nor complete (N). Examples of these coded responses to activity question 1 for each of the three reactions are shown in Figure 3.12 -Figure 3.15.

Table 3.35. Percentages of student responses characterized by correctness and completeness.

Pre-lab Activity Question	C&C	C	SC	N
Activity Question 1. Depict microscopically the chemicals before and after the reaction for the assigned reaction.	39%	22%	11%	28%
Activity Question 2. Explain briefly how the flow of heat allows you to observe the enthalpy and temperature changes in these reactions.	17%	44%	6%	33%
Activity Question 3. Based on your observation, explain why hot coffee is usually put in Styrofoam cups rather than glasses.	72%	6%	6%	16%

Activity Question 1 Responses:

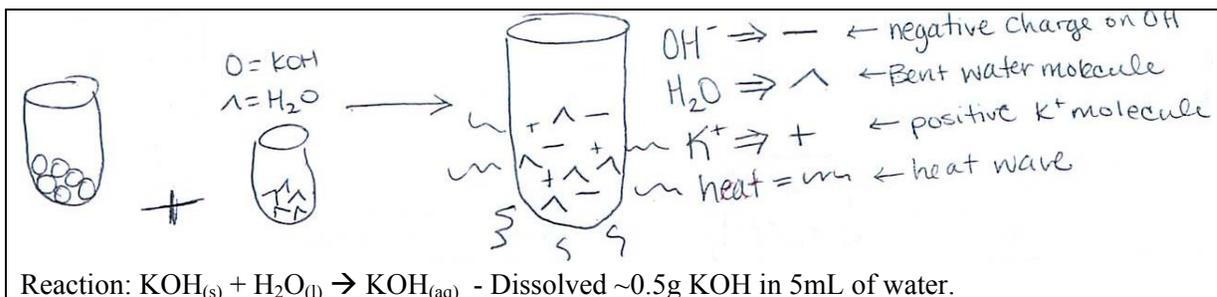


Figure 3.12. Sample of the C&C response for activity question 1.

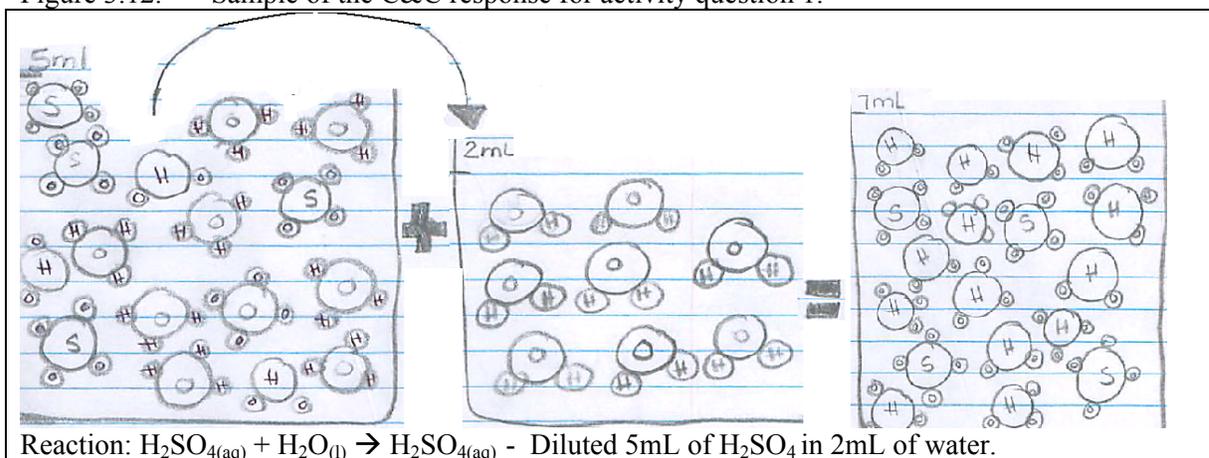


Figure 3.13. Sample of the C response to activity question 1 with incorrect water structure.

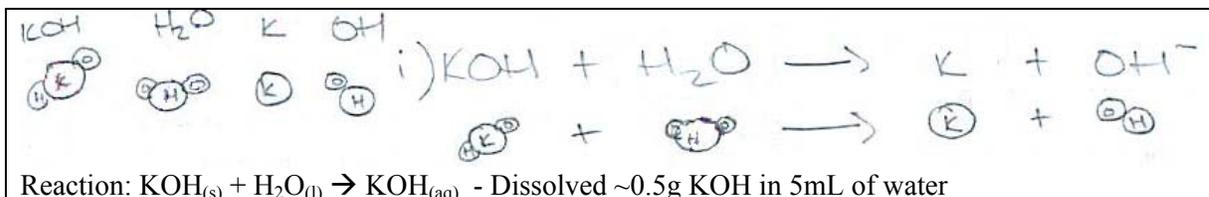


Figure 3.14. Sample SC response with incorrect structures and charges to activity question 1.

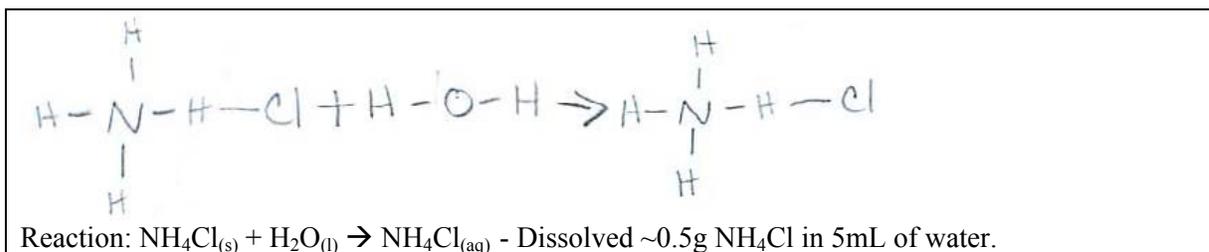


Figure 3.15. Sample of the N response to activity question 1 showing incorrect Lewis structure and an inappropriate response to the question.

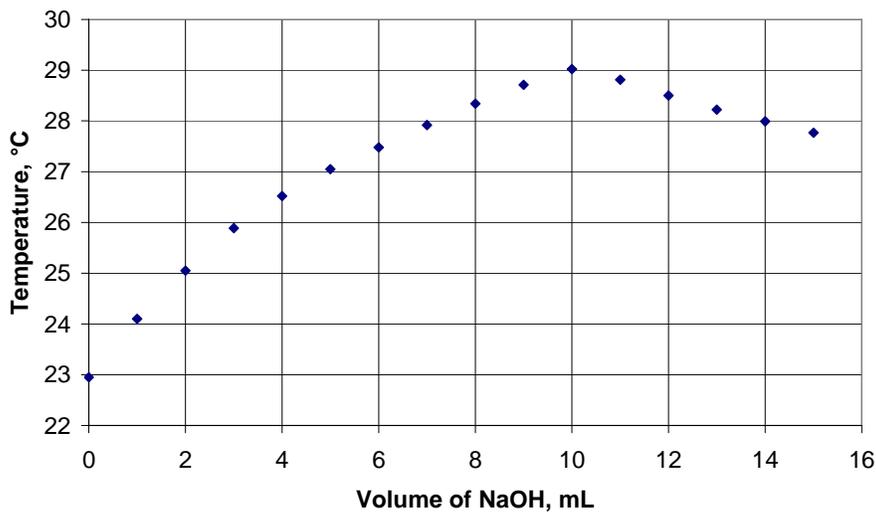
A colorimetric titration (phenolphthalein) was demonstrated to the FS students prior to the experiment, allowing students to observe a different titration method. Students made comparisons to the thermometric titrations, as well as observed conditioning and use of titration glassware (psychomotor information) (Table 3.36). Students' opinions on each method included: 1) colorimetric can be done slower while thermometric titrations need to be done swiftly to prevent temperature loss, 2) monitoring temperature is more quantitative while monitoring color is qualitative, or 3) observing color may be difficult particularly for students with visual problems.

Table 3.36. Percentage of thoughtful responses related to the demonstration.

Action	Percentage of students	Mental operation
Compared titration methods (thermometric vs. colorimetric).	56%	Matching and specifying
Suggested potential advantages and disadvantages of each method.	53%	Examining importance and matching

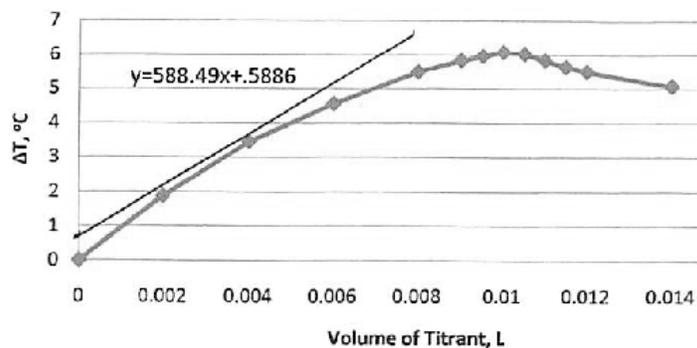
Students then performed the thermometric titrations to monitor the progress of acid-base (NaOH, HCl and HNO₃) and redox titrations (Fe²⁺ and MnO₄⁻). Multiple trials of each titration were performed, where the first trial of each titration was done incrementally (~1mL at a time) to identify the volume range where the inflection was observed. Students repeated the titration, adding the titrant in smaller increments within this volume range to obtain a more precise value. Students drew and extrapolated thermograms (Graph 3.13) and used the graphs to determine end points in order to calculate the unknown concentrations of the analytes using Graph 3.13. Students were expected to decide the number of data points needed to collect useful data.

Student data: Volume vs. Temperature, °C



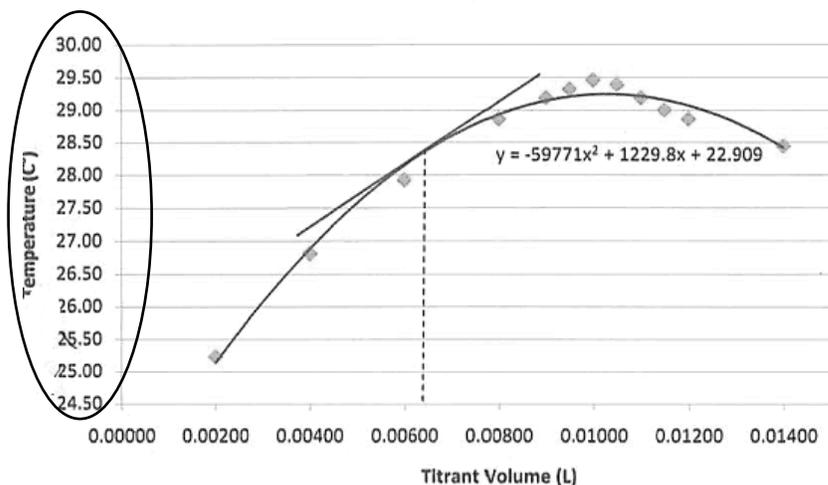
Graph 3.13. Thermometric titration graph for NaOH vs. HCl.

SS students were assigned one of the two methods for determining ΔH_n by deriving the slope of the curve (Equation 3.5): Methods A (Graph 3.14) and B (Graph 3.15). Students needed to be reminded that the volume used to determine ΔH_n must be in liters (x-axis) and the y-axis is the change in temperature, rather than just the temperatures obtained during the titration (Graph 3.14). Eight of the twelve SS students (67%) who obtained the enthalpy of neutralization graphs and performed the calculations were able to correctly derive the estimated ΔH_n of the reaction of NaOH with HCl.



Graph 3.14. Student thermometric graph using Method A.

**Trial 2, Titration of 1.0M HCl with 1.03M NaOH
Titrant Volume (L) vs. Temperature**



Graph 3.15. Student thermometric graph using Method B.

FS LLR questions were evaluated after the pilot implementation. Some FS questions were replaced with questions that directly assessed misconceptions (FS questions 1 and 2 for SS questions 1 and 4), while others were modified to include diagrams relating the concepts queried (Table 3.37). Students reflected on and utilized thermometric titration data to answer conceptual questions, where the students identified what influenced or affected their observation of the acid-base titrations (FS-Question 1 and 2, analysis skill and metacognition thinking), rationalized their observations (FS- Question 3, generalizing skill), depicted the titration at the molecular level (SS-Question 1 page 177, symbolizing, comprehension and knowledge utilization skill) and made extensions (applications to new situations, SS-Question 2, making decisions skill). It was observed that SS students who understood and were able to explain heat flow and temperature changes in the pre-lab activity (C&C and C responses) were better able to make connections between the titration and thermochemistry in post-lab conceptual questions. These students specifically referenced the pre-lab activity when answering the questions.

Table 3.37. Percentages of student responses characterized by correctness and completeness for similar questions used in both implementations.

Post-lab question and skill required	FS Students				SS Students			
	C&C	C	SC	N	C&C	C	SC	N
Question 4. Rationalize shape of titration graph based on psychomotor information (analysis)	22%	41%	0%	38%	28%	50%	11%	11%
Question 5. Diprotic acid thermometric titration graph (knowledge utilization)	66%	0%	0%	34%	39%	22%	22%	17%

FS Post-lab Question

1. What other factors influence the evolution of heat in the acid-base reactions; give at least 2 reasons? (Hint: you are not adding just pure acid or pure base to each other).
2. What can be done to account for the errors you have noted in your answer to question 1?
3. Rationale for enthalpy change in redox reactions (analysis)

SS Post-lab Question 4: What would happen to the temperature if 1mL portions of HCl solution had been added to NaOH, instead of the way the experiment was performed? Sketch the expected graphs.

Students were able to correctly rationalize the shape of the thermograms, however the majority of the students did not explain the post reaction slope (post-lab question 4, Table 3.37). The difference in the percentages of the coded responses to post-lab question 5 between the FS and SS students is attributed to the incorporation of pictorial representations (Table 3.37). The diagrams better assessed students' understanding of the acid-base concepts as it related to the experiment. Examples of responses characterized as C&C, C, SC and N are shown in Figures 3.16-3.20.

Sample C&C Response: “If HCl were added to NaOH in 1 mL portions instead of NaOH being added to HCl, the same reaction would occur. The chemical reaction is still the same. The temperature will increase when HCl is added until you have reached the endpoint, then it will decrease b/c of excess HCl.”

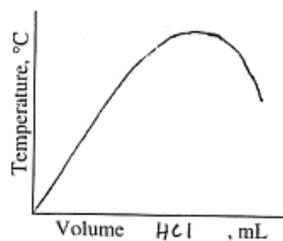


Figure 3.16. Sample C&C response for the reversal of the order of addition of reagents.

Sample SC Response: “The graph would be more precise in 1 mL increments than when done in 10 mL increments.” (The answer does not address the question asked and the diagram is SC but does not reflect response).

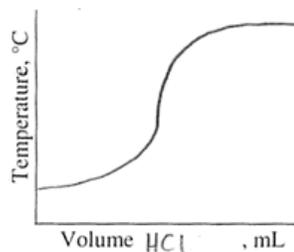


Figure 3.17. SC diagram for the reversal of the order of addition of reagents.

Sample N Response: “Temperature would have decreased as the titrant was added, endothermic reaction.”

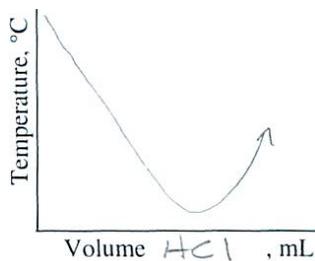
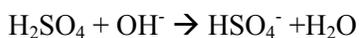


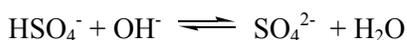
Figure 3.18. Incorrect reverse addition diagram.

SS Post-lab-Question 5: Draw the expected curve for a diprotic acid (2 ionizable protons)? Briefly, rationalize the shape of the graph.

Sample C&C Response: “A diprotic acid, such as H₂SO₄, would experience two endpoints. One for each reaction of



and one for



After the first endpoint has been reached the temp [temperature] shortly decreases than increases again because HSO₄⁻ is reacting. The temperature of the second endpoint is higher because it is harder to remove a proton from HSO₄⁻ than H₂SO₄.

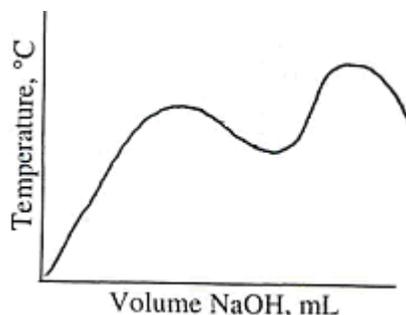


Figure 3.19. Sample C&C response to post-lab question 5.

Sample N Response: “It would be much like HCl + NaOH. Because the salt would form & it would be exothermic.”

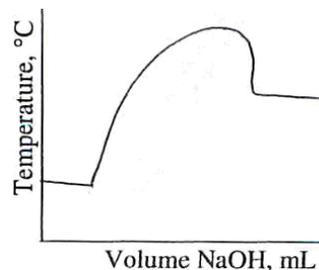


Figure 3.20. Sample N response for pictorial representation of diprotic acid titration

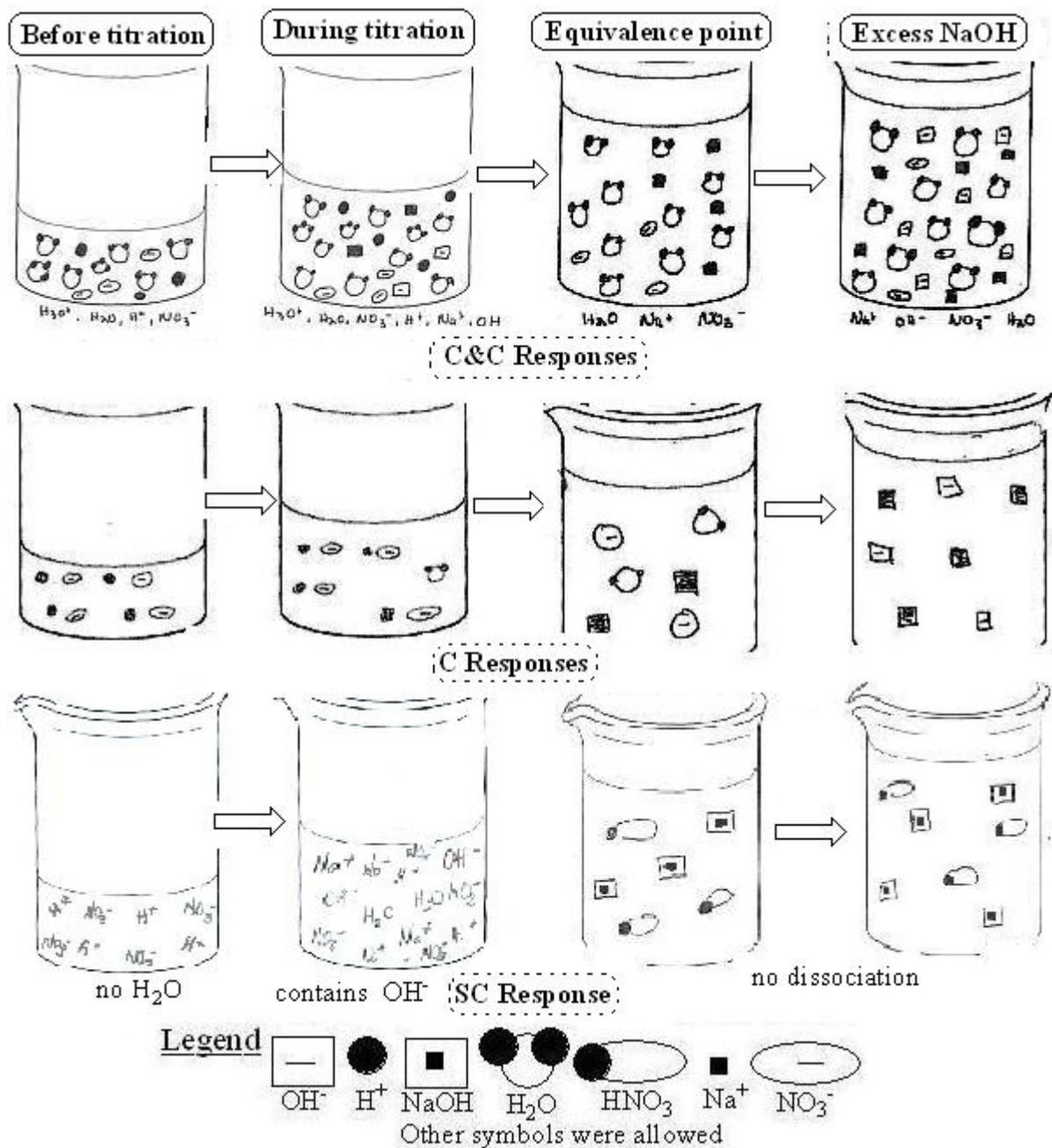


Figure 3.21. Sample pictorial representations of the titration for post-lab question 1.

Students' reflection on the pre-lab questions demonstrated gains in knowledge for each question before and after the experiment (Table 3.38).

Table 3.38. Score changes for pre-lab questions after reflection.

Pre-lab questions and skill needed	Initial				Review			
	C&C	C	SC	N	C&C	C	SC	N
Question 1: Acid base strength (symbolizing and integrating) page 163.	74%	11%	0%	16%	84%	5%	0%	11%
Question 2. Calculation using diagrams, including correct use of significant figures (integrating) page 171.	21%	21%	16%	42%	74%	16%	5%	5%
Question 4: Determine conjugate pairs (recognize).	42%	26%	21%	11%	79%	16%	0%	5%
Question 5: Calculate c_t (problem solving).	0%	0%	0%	100%	32%	0%	0%	68%

A summary of problems observed from the students' responses to the activity, post-lab and demonstration questions accompanied by some examples, with suggestions for future implementations and modifications already made to the lab are presented in Table 3.39.

Table 3.39. Problems observed during the implementations with relevant suggestions and modifications.

Problem Area and Examples	Modifications/Suggestions
Pre-lab Activity	
1. Conversion of symbolic language of the equation to symbolic representations and depiction of dissolution, dilution or enthalpy. - 28% of students wrote the chemical equations in the flask to represent the reactions or provided no response. - Only three students utilized their drawings to depict enthalpy changes and heat transfer (Figure 3.12).	- Provide greater connection from the activity to the thermometric titrations - Additional observations of laboratory items to infer heat transfer from items other than chemical changes. - Make better connections to the thermochemistry concepts to better explain insulators, conductors and energy flow.
2. Conversion of symbolic language to Lewis structures. - Figure 3.14 and Figure 3.15	
3. Inability to completely explain chemical phenomenon, particularly activity question 1 and 2. - "If heat flows from the solution to your hand then its releasing heat & ΔH is (-). If heat flows from your hand to the solution then you know its absorbing heat & ΔH is (+)." (C response).	
4. Inability to extend concepts from observations to applications. - Styrofoam cup[s] keeps heat in better than glasses." (SC response).	

Table 3.39. Problems observed implementations with relevant suggestions and modifications (continued).

Problem Area and Examples	Modifications/Suggestions
Colorimetric titration demonstration	
1. Comparison between colorimetric and thermometric titrations. - Colorimetric change was thought to indicate the end of the reaction, while inflection point indicates the reaction is still occurring.	- Provide greater connection between the demonstration and the experiment. - Provide brief explanation of the differences between endpoint indicators at the molecular level.
2. Understanding of the titration at the molecular level. - Colorimetric change is equivalent to pH changes (not a response to a specific pH range) or that indicator is added to promote the reaction reaching equilibrium.	- Post-lab question 1 required students to depict the reaction at the molecular level.
Calculations and Problem solving	
1. Extrapolation endpoint from the thermogram and use of tangents for Methods A and B to determine ΔH_n . - Picking a value on the thermogram as the endpoint rather than extrapolate endpoint.	- Brief review of mathematical strategies demonstrating proper use of these methods. - Pre-lab questions requiring extrapolations.
3. Significant figures posed a problem even though sample answers were provided in the pre-lab question. - Students who incorrectly used significant figures did not correct their responses after the re-evaluated pre-lab.	- Direct students to one source for determining significant figures.
4. Determination and strength of conjugate pairs - Wrong products for acid-base equations. - Number of students who correctly identified the conjugate pairs and their strength was low Table 3.38	- Require demonstration of how conjugate pairs were derived. - Revised questions.

Complete analysis of the students' Responses, sample answers, and complete questions are provided in Appendix F.

3.6 Olfactory Titration

Glucosinolates, or S- β -D-glucopyranosyl Z-thiohydroximoyl-O-sulfate esters, are water-soluble anions containing an S-glucoside linkage to a sulfated ketoxime with different aglyconic side chains (Figure 3.22) (192,194,195). They are found in Cruciferea plants including Brassica vegetables such as mustard, radish, cabbage, Brussels sprouts, broccoli, and rutabaga (swede). Substances derived from these glucosinolates are used by the plant as natural pesticides and are also responsible for the bitter or sharp taste. The rutabaga (*Brassica napobrassica*) is a root vegetable that contains particularly indole glucosinolates, (196,197) which can be hydrolyzed to isothiocyanates, nitriles and thiocyanates in the presence of water by the enzyme myrosinase (β -thioglucoside glucohydrolase) by cleaving the glucose group. The isothiocyanate produces the characteristic aroma of the vegetable and is the common product of the hydrolysis reaction (198,199), while thiol compounds, specialized proteins and ferrous ions in the medium can facilitate the formation of nitriles and thiocyanates rather than isothiocyanates (200). The myrosinase and glucosinolates are stored in separate compartments of the cell to prevent damage to the plant, and come together under conditions of physical injury (201).

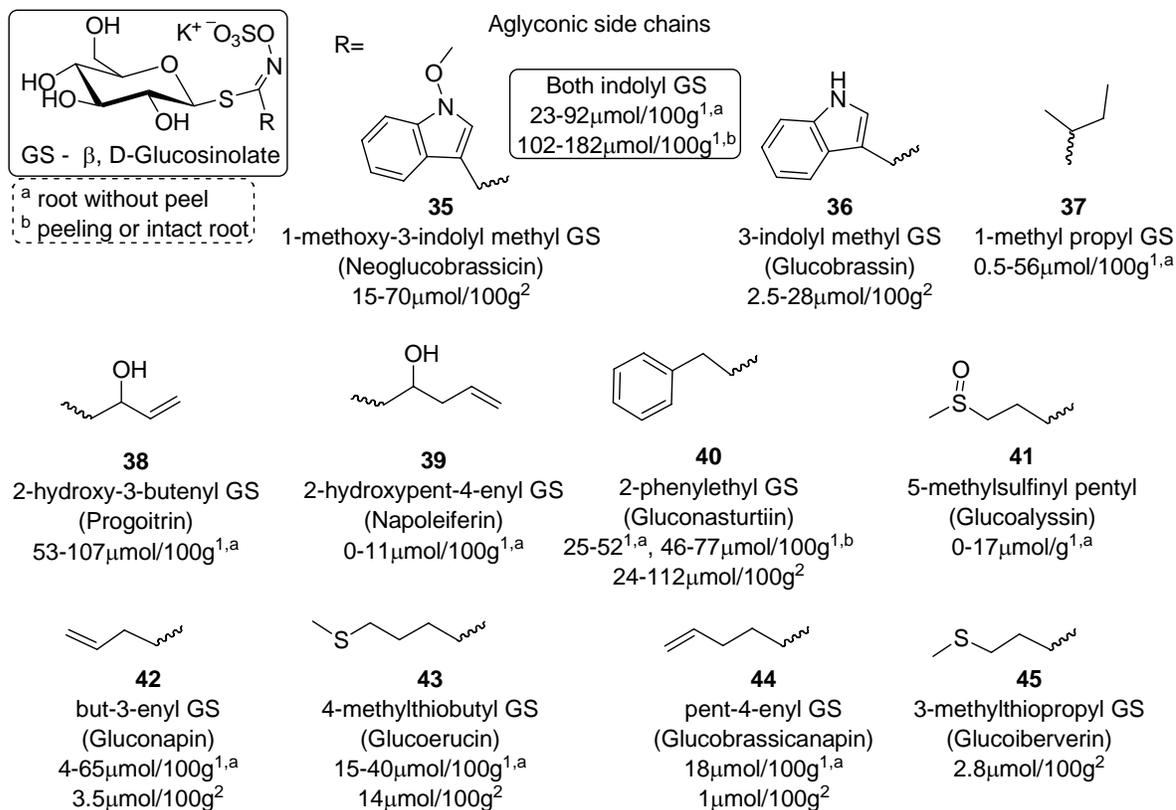


Figure 3.22. Aglyconic side chains with average content of rutabaga glucosinolates.

¹Carlson et al.; ²Hopkins et al. (195).

In the absence of the enzyme, glucosinolates can be hydrolyzed at low pH. The literature points out that the enzyme could be denaturalized by heating ('cooking' the vegetable) to temperatures higher than 80°C for 10 minutes (202). Cooking of brassica vegetables such as the rutabaga causes myrosinase to be denatured allowing for glucosinolate hydrolysis by acidic medium. These facts were exploited in this experiment to utilize glucosinolates as olfactory indicators.

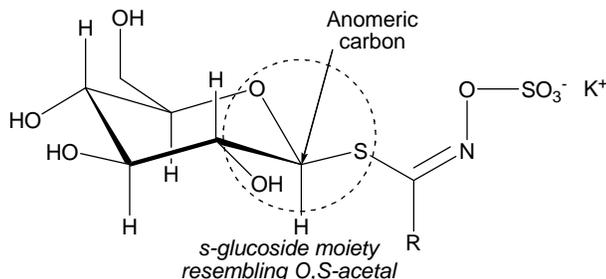
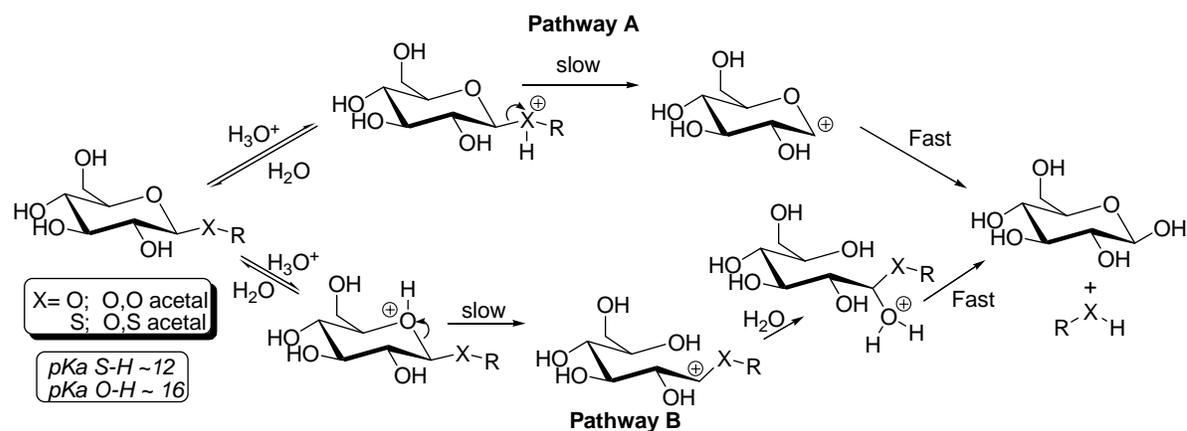


Figure 3.23. Generic structure of glucosinolate showing anomeric carbon resembling *O,S*-acetal.

The anomeric carbon of the glucosinolate resembles an *O,S*-acetal in which either the C-O or C-S can be cleaved first in the hydrolysis mechanism (Figure 3.23). The mechanism for this *O,S*-acetyl hydrolysis is uncertain (Scheme 3.9) and generally of great debate in the literature (203), however, one pathway seems to be preferred over the other under various circumstances (204,205). Clayton et al. have shown that anomerization and contraction from a six- to a five-membered ring occurred at the same time during hydrolysis of 1-methyl thioglycosides demonstrating that C-O cleavage must be competitive or faster relative to C-S cleavage (203). Conversely, Fife and Anderson have shown that the acid-catalyzed solvolysis of benzaldehyde *O*-methyl *S*-phenyl acetal in 2-propanol occurs with the sulfur being protonated and subsequently a C-S cleavage. The neighboring oxygen would stabilize the oxocarbenium ion intermediate better than would sulfur and they suggest that C-O bond breaking was less likely but was not excluded (206). Bamford et al. have also suggested, based on kinetics studies that the hydrolysis mechanism for 1-thio- β -D-glycopyranosides occurs via a cyclic oxocarbenium ion (Scheme 3.9, Pathway A) (207).



Scheme 3.9. Potential mechanisms for *O,O*- or *O,S*- acetal acid-catalyzed hydrolysis.

The Pathway A requires that the reaction be catalyzed only by hydronium ion and involves C-S bond-cleavage in the rate-limiting step to give the oxocarbenium ion and aglycon (R-X groups

in Figure 3.22 attached to the pyranose as shown in Scheme 3.9). Pathway B involves the rate-limiting step as the ring opening (204,208). The likely pathway could be attributed to the structure of the molecule considering electronic and resonance factors. Lartey and Fredor have shown that the hydroxyl group on C-2 of the pyranose on the pyranose ring influenced the mechanism by which the hydrolysis proceeded. Purin-6-yl-1-thio- D-glucopyranoside **46** proceeded via the Pathway A, while purin-6-yl-2-deoxy-1-thio-D-glucopyranoside **47** proceeded via another pathway similar to pathway A, where the mechanism involves the rate limiting proton transfer to the sulfur (first step of the mechanism) which is followed by the C-S bond cleavage, rather than the rate limiting step of Pathway A being the C-S bond cleavage (204). De and Fife have shown using kinetics studies that 2-(*p*- phenyl)-1,3-oxathiolanes (**48**) undergoes hydrolysis by pathway B (209).

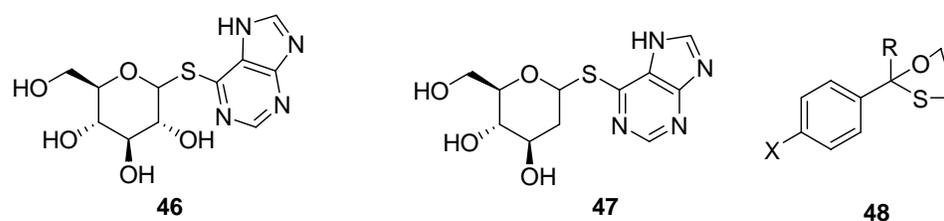


Figure 3.24. Purin-6-yl-1-thio-D-glucopyranosides (204) and oxathiolanes (209) used to determine hydrolysis mechanism.

From studies on the hydrolysis of benzaldehyde *O,S*-acetals, electron-withdrawing substituents (EWG) on the thiol increase the amount of C-S cleavage, while electron-donating substituents (EDG) on the benzaldehyde increase C-O cleavage (210). The bond cleavage would be moderated by the electronic pull exerted by and basicity of the sulfur leaving group as well as the electronic push exerted by the remaining molecule. Molecules **49b** and **50c** promoted C-O cleavage, **49c** and **50a** promoted both C-O and C-S cleavages competitively and C-S is promoted in **49a**. It was inferred that electron donation by alkyl groups (A) on the glucopyranose (**51**) of the glucosinolate and electron withdrawal (B) on the thiol can increase C-O cleavage. The alkyl groups could promote the carbocation formation by stabilization, facilitating the sulfide as a leaving group. The ketoxime-

like group re-enforced with the sulfate group could provide electron withdrawal from the sulfur, to facilitate the C-S cleavage (Figure 3.25).

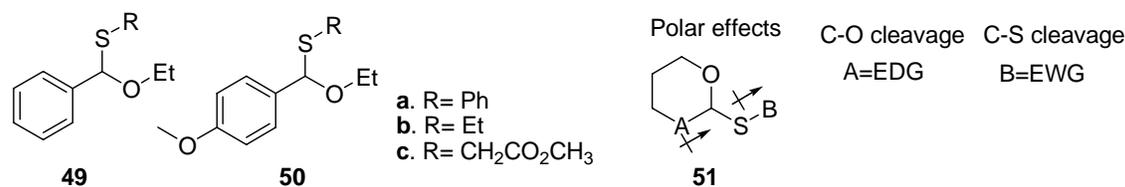


Figure 3.25. Polar effects with attached groups.

The resonance effect due to the sulfated ketoxime group of the glucosinolate could contribute to the stability of the leaving group (thio methyleneamino sulfate) (Figure 3.26). Due to the resonance and polar effects it can be inferred that the mechanism could occur through the promotion of the C-S cleavage.

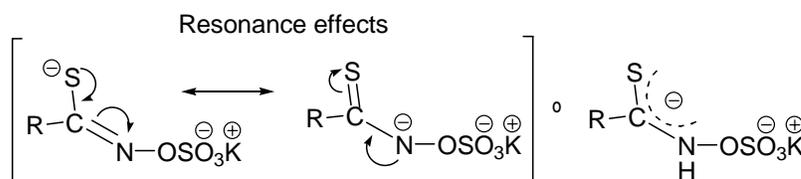
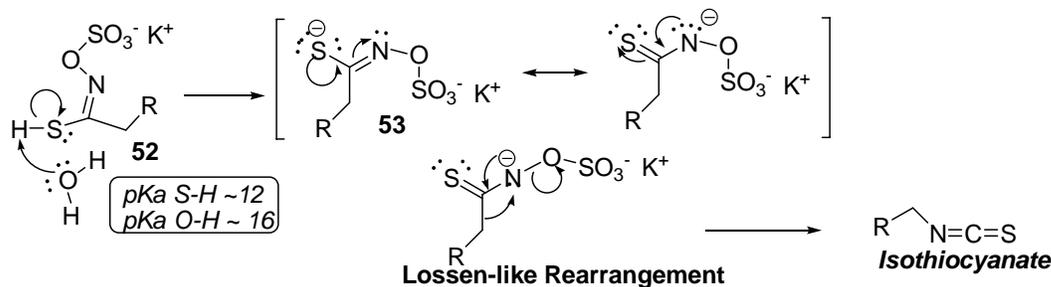
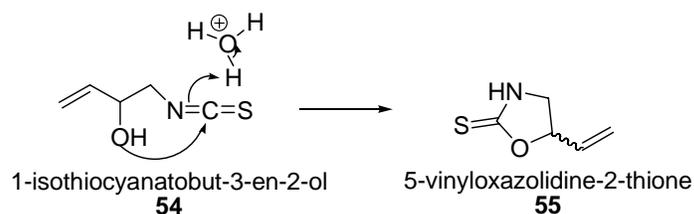


Figure 3.26. Resonance effects of leaving group on the hydrolysis mechanism.

Both mechanisms result in the same mercapto sulfated ketoxime **52**, which is easily deprotonated to sulfonatoxyimidothioate **53** (Scheme 3.10). This final step involves a Lossen-like rearrangement (Scheme 3.10), which typically is the treatment of *O*-acylated hydroxyamic acids with base to give isocyanates, and is also postulated to occur in the enzymatic hydrolysis (211,212). The majority of the glucosinolates consists of the aromatic, indolyl and β -hydroxyl. However, isothiocyanates formed from β -hydroxyl glucosinolates (**54**) are unstable and spontaneously cyclize to the oxazolidine-2thione, **55** (Scheme 3.11) (213,214). The aroma of the rutabaga would therefore consist of the indolyl, aromatic and aliphatic glucosinolates hydrolyzed to the isothiocyanate species.

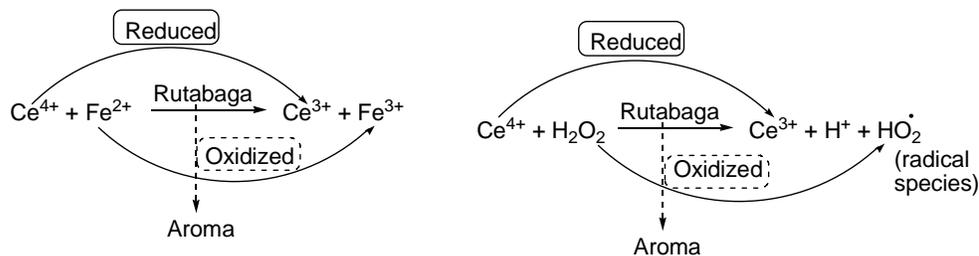


Scheme 3.10. Final step of both mechanisms - Lossen like rearrangement to form the isothiocyanate.



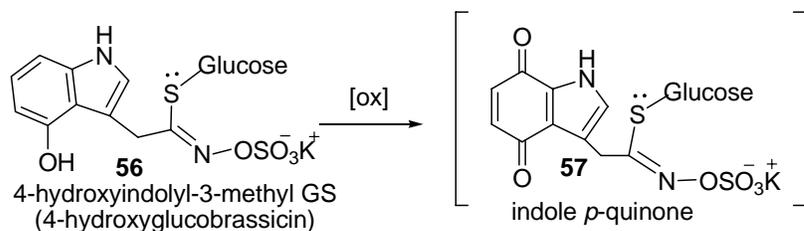
Scheme 3.11. Breakdown product of β -hydroxyl isothiocyanate.

The rutabaga vegetable was also utilized in redox titrations where the aroma produced at the endpoint of the titration is different from that of the acid-base titration. This experiment was attempted on account of a literature proposal that stated the vegetable appeared to have reducing properties (215). Brassica vegetables exhibit antioxidant properties which have been attributed to the ability for cancer modulation decreasing the risk of cancers (216). This activity has been reported to be a result of glucosinolate hydrolysis products implicated in anticarcinogenic mechanisms. Based on this finding, a few researchers have explored further the potential mechanism of this oxidation. From these studies, the mechanism of the oxidation of the rutabaga indicator solution is speculated as shown in Scheme 3.12. From the literature, various products or intermediates for this oxidation can be speculated and may vary depending on the side chains. Oxidation at R-groups or at the mercapto sulfated ketoxime of the glucosinolate or a combination of these oxidation products may also be present.

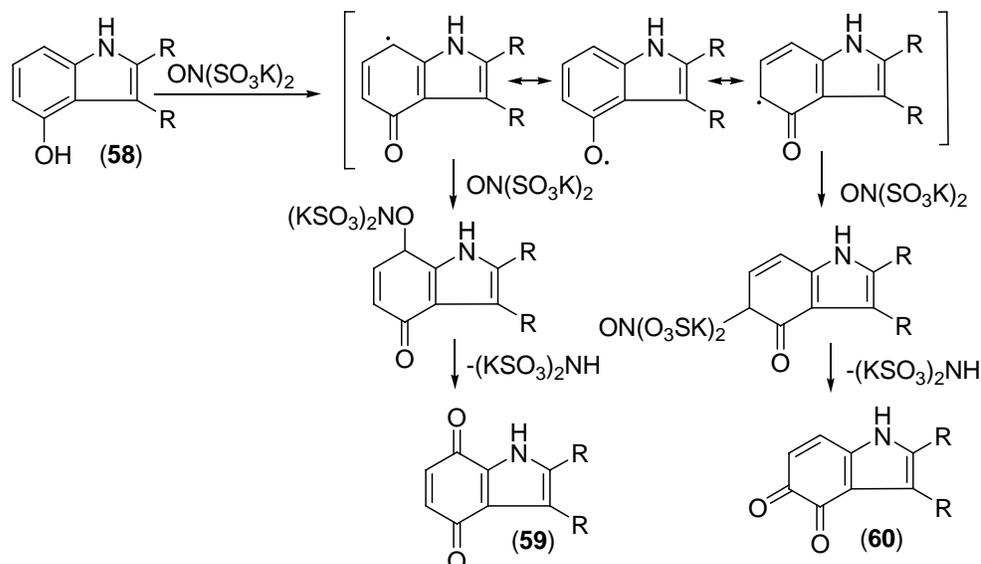


Scheme 3.12. Redox reaction using CAN (Ce^{4+}) with Fe^{2+} and H_2O_2 .

Research suggests that the oxidation of the glucosinolate occurs at the side chain of the molecule. Truscott and Mantley investigated the mechanism of oxidation of 4-hydroxyindolyl-3-methyl glucosinolate (4-hydroxyglucobrassicin, **56**) using 4-hydroxyindole as a model compound and have shown by trapping the intermediate with aniline that the mechanism takes place via an indole *p*-quinone intermediate, **57** (Scheme 3.13) (217). In the redox titration, a white precipitate is formed (similar results shown in the literature) in addition to the aroma. The oxidation of various hydroxyindoles (**58**) has been reported in the literature to occur, particularly with the use of Fremy's salt (dipotassium nitrosodisulfonate) in the 1950's to 70's to give quinines, **59** and **60** (Scheme 3.14) (218). It can be inferred that similar structures can be obtained by the oxidation of the hydroxyindole glucosinolates.

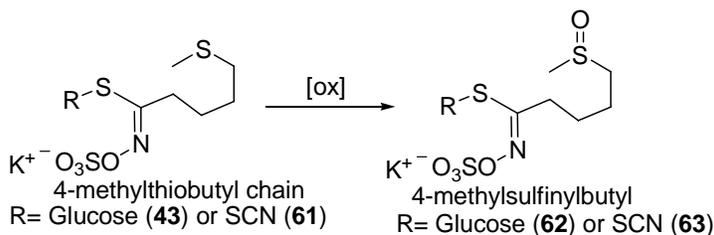


Scheme 3.13. Proposed intermediate for redox titration for indole glucosinolate.



Scheme 3.14. Proposed mechanism for the oxidation of the hydroxyindoles using Fremy's salt.

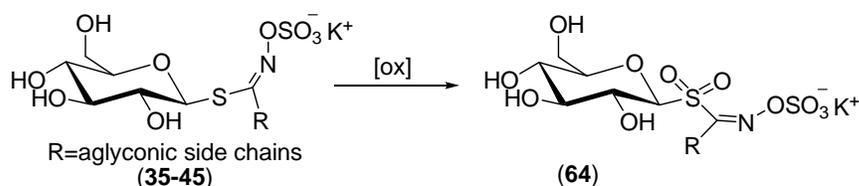
Barillari et al. have also shown that the sulfide side chains of the glucosinolate (**43**) and isothiocyanates (**61**) are oxidized to sulfinyl groups, **62** and **63** (219). Sulfides can be oxidized to sulfoxides which can further be oxidized to sulfones. These oxidation products may create the difference in aroma observed in the redox titration. The generation of acid from the use of peroxide as an oxidant in the redox titration (Scheme 3.12) or the inclusion of a small amount of acid would promote the hydrolysis of the glucosinolates (**27**) to give the new isothiocyanate products (**29**) (Scheme 3.15).



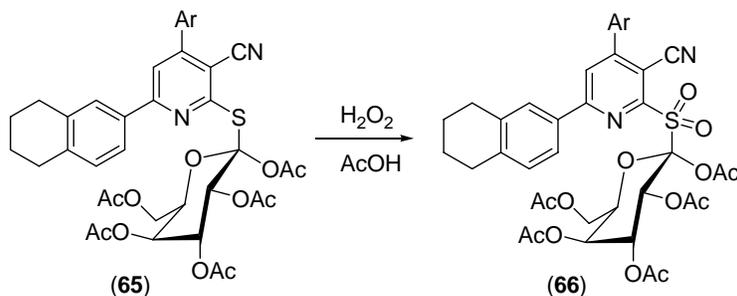
Scheme 3.15. Oxidation of sulfide side chain to produce sulfinyl groups.

The sulfide at the anomeric carbon of the glucose moiety may also be oxidized to a sulfone, **64** (Scheme 3.16). Khalifa et al. have oxidized acetylated *s*-glycoside (**65**), *s*-galactoside, *s*-xyloside

and *s*-arabinoside with H₂O₂ in acetic acid to afford the corresponding sulfone (**66**) (Scheme 3.17). The *s*-pyridyl glycosides were synthesized from the *s*-alkylation of pyridine-2-thione with D-glucopyranosyl bromide (**220**). Baker has shown an oxidation of a thioacetals carbohydrate with lead tetraacetate to sulfones (**221**). Similarly, sugars such as glucose and furanose and the derivatives (*o,o*-glycosides) have been shown to be oxidized to form 4-*o*-formyl arabinose with Ce (IV) (**222**), to CO₂, oxalic acid and acetic acid with alkaline permanganate (**223**), to lactones with an oxoammonium salt (**224**) and to diol monoesters with molecular oxygen (**225**).



Scheme 3.16. Oxidation of sulfide at the anomeric carbon.



Scheme 3.17. Oxidation of sulfide of *s*-pyridyl glycoside.

Experimental overview

The challenges of this project were to develop a method of rutabaga preparation and proper utilization of the extract for its use in an olfactory titration. Various methods were attempted to utilize the rutabaga as an indicator. With all the methods, the vegetable was heated to denaturalize the myrosinase enzyme before extraction of the glucosinolates. Fresh rutabagas from local grocery stores are always covered in a waxy film to preserve freshness. This film was either removed by

scratching off the wax which may result in some residual wax on the surface or by peeling the vegetable. These vegetables typically weigh 0.5-1 kg and were usually cut into 4-6 equal sections to be used for each extraction method. The rutabaga sections were cut into smaller cubes approximately 2 cm in length. To denature the myrosinase, the cubes were either boiled or heated in an oven. To boil the cubes, a beaker of 1% NaCl-D.I. water solution was brought to a boil, as the added cold rutabaga generally drops the temperature closer to 80-90°C. The rutabaga was heated between 80-100°C for ten minutes, after which the vegetable was removed and allowed to cool. The rutabaga cubes may be heated in an oven to completely or partial dryness between 80-100°C.

The first promising method employed was to soak slices or crushed pieces of the “cooked” vegetable in ethanol for a period of 10 minutes and decanting (Method A). The decanted solution was used as the olfactory indicator by adding it to the NaOH solution. At the endpoint, the small excess of acid begins the hydrolysis of the olfactory indicator, which was inhibited in the base with the absence of the enzyme. Other extraction methods utilized the Soxhlet apparatus to extract and rotoevaporation or distillation to remove the solvent to give a concentrated extract which was used as the titration indicator. The vegetable sample was boiled only for Method A, while the other methods used both boiling and oven heating.

Methods B and C involved the use of a Soxhlet extractor which enables solids to be extracted with fresh warm solvent by continually circulating the warm solvent over the solid. The solvents used were methanol and ethanol. The solids were placed in a cellulose thimble inside the Soxhlet apparatus and solvents were allowed to reach boiling in order to circulate in the apparatus for approximately 3 hours. The apparatus was then allowed to cool and the solvent was removed by fractional distillation (Method B) or rotoevaporation (Method C). The resulting product was either a dark brown viscous solution or a creamy-like solid, respectively, depending on the amount of

residual solvent or water present in the sample. Five drops of the liquid or five drops of the solid added to a small amount of methanol were used in the titration (Table 3.40).

Table 3.40. Titration using the rutabaga indicator (Method A) compared to various indicators.

Indicator	pH of the Change	Final volume of HCl
Bromothymol Blue	6.93	3.60 mL, \pm 0.05 mL, $n=3$
Methyl Red	4.59	3.75 mL \pm 0.05 mL, $n=3$
Phenol Red	7.28	3.65 mL \pm 0.05 mL, $n=3$
Phenolphthalein	8.65	3.60 mL \pm 0.0 mL, $n=3$
Rutabaga	6.58	3.58 \pm 0.05 mL, $n=4$
Standardized solutions: HCl 0.278M; 0.205M NaOH (5.00 mL)		

The heating processes showed no significant impact on the results, as accurate results were obtained by all three processes. However, the sample from the completely oven dried rutabaga extracted with methanol also produced a change in color at the end point of the titration. Samples obtained from Method C (rotoevaporation) produced the most accurate results, possibly because less volatiles or compounds may be lost using the rotoevaporator. Different extracts had slightly different aromas at the end point, however, each still was recognizable as the rutabaga aroma. This could be a result of selectively extracting various glucosinolates or preference for various glucosinolates by each method or solvent. Titrations performed with the rutabaga extracted Methods B and C (Soxhlet extraction) were more accurate and produced stronger aroma than those performed using the rutabaga crushed in ethanol which may be due to a higher concentration of glucosinolates. Overall, the titrations using all of these methods have been accurate and the data reproducible. Rutabaga results are compared with traditional indicators such as phenolphthalein, phenol red, bromothymol blue and methyl red for Method A in Table 3.40, and with phenolphthalein for Methods A-C in Table 3.41.

Table 3.41. Titration of NaOH vs. HCl using the rutabaga indicator (Methods A-C) compared to standardized concentration using phenolphthalein. * Color change observed.

Extraction Method	Heating Process	<i>n</i> , samples	Calculated Concentration (Rutabaga)	Standardized Concentration (Phenolphthalein) ± 0.01 M, <i>n</i> =3
A: EtOH + Crushed	Water Bath	<i>n</i> = 3	0.222 ± 0.011 M	0.229 M
B: EtOH + Soxhlet + distillation (BP>100°C)	Water Bath	<i>n</i> = 10	0.226 ± 0.004 M	0.223M
	Partially oven dried	<i>n</i> = 10	0.244 ± 0.004 M	0.249 M
	Completely oven dried	<i>n</i> = 9	0.227 ± 0.004 M	0.223 M
C: EtOH + Soxhlet + rotoevaporation	Water Bath	<i>n</i> = 10	0.211 ± 0.003 M	0.208 M
	Partially oven dried	<i>n</i> = 7	0.269 ± 0.009 M	0.272 M
	Completely oven dried	<i>n</i> = 10	0.254 ± 0.006 M	0.254 M
B: MeOH + Soxhlet + distillation (BP > 80°C)	Water Bath	<i>n</i> = 8	0.200 ± 0.005 M	0.208 M
	Partially oven dried	<i>n</i> = 10	0.268 ± 0.004 M	0.272 M
	Completely oven dried*	<i>n</i> = 4	0.242 ± 0.005 M	0.250 M
C: MeOH + Soxhlet + rotoevaporation	Water Bath	<i>n</i> = 10	0.222 ± 0.006M	0.223 M
	Partially oven dried	<i>n</i> = 10	0.112 ± 0.001 M	0.112 M
	Completely oven dried *	<i>n</i> = 9	0.226 ± 0.006 M	0.223 M

A method similar to Method A used in the acid-base experiment was used to develop the redox indicator was obtained by soaking the boiled rutabaga in the reducing agent solutions ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and H_2O_2 for approximately 10 minutes (method D). The resulting solution was then measured out into the desired quantity and titrated against the oxidizing agent ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (CAN). Other reagents (KMnO_4 , $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{Fe}(\text{NO}_3)_3$, KI and $\text{K}_2\text{S}_2\text{O}_3$) were attempted, but the results have not been as successful. It was important not to use reagents that require an acidic medium to react in order not to hydrolyze the rutabaga with the added acid, and provide a competing reaction which alters the results. The aroma produced was different from that of the acid-base titration, but very distinctive. The rutabaga indicator was oxidized producing an aroma at the endpoint of the redox reactions shown in Scheme 4. The data obtained using method D (Table 3.42) shows that the redox titration using the rutabaga indicator is reproducible and comparable to

that of colorimetric indicators ferroin and sodium diphenylamine-4-sulfonate (Table 3.42). As with the acid-base titration, the endpoint of the titration is observed when the aroma is present at the time when excess oxidizing agent is present in the titration mixture.

Table 3.42. Redox indicators (n=3 trials) compared against the rutabaga indicator (CAN vs. Fe^{2+} and H_2O_2) using method D.

Reducing Agent	Redox Indicator	Average Final Volume	[Solution Titrated]
Fe^{2+}	Ferroin	5.60mL \pm 0.05 mL	0.0885M \pm 0.0010 M
	Rutabaga	5.72 \pm 0.14 mL	0.0875 \pm 0.0022M, n=10
H_2O_2	Ferroin	4.65mL \pm 0.05 mL	0.108M \pm 0.0010 M
	Rutabaga	4.76mL \pm 0.20mL	0.105 \pm 0.004M, n=10

When similar procedures to acid-base titration methods B and C were used for the redox titration, the aroma appeared very faint and therefore gave inconsistent results. The faint aroma with these methods may be a result of the volatility of the glucosinolates that are oxidized or the slow or little hydrolysis of the oxidized form of glucosinolate to the corresponding isothiocyanate due to the method of preparation of the indicator.

The complete mechanisms of the C-O and C-S cleavages are given in the appendices. The olfactory titrations were successfully performed by two undergraduate students as part of the testing. These students were able to establish and calculate the molarity as accurately as in colorimetric and potentiometric. An experimental procedure for students to be used with the LLR is given in the appendices and may be used for implementation of the experiment. Pre- and post lab questions are also suggested which were developed neutralization, acid-base properties, redox and calculations misconceptions. In addition, future experiments should explore the use of the rutabaga peel in making the indicator as it contains a high concentration of indole glucosinolates, as well as other brassica vegetables may be compared.

REFERENCES

1. Zuberick, J.W. *J. Chem. Edu.* **1992**, *69*, 387.
2. Felder, R. M. *J. Chem. Edu.* **1996**, *73*, 832-836.; D'Arcy, C. J.; Eastburn, D. M.; Bruce, B. C. *College Teaching*, **2009**, *57*, 56-63.; Dunn, R.; Honigsfeld, A.; Doolan, L. S.; Bostrom, L.; Russo, K.; Schiering, M. S.; Suh, B.; Tenedero, H. *J. Educ. Strategies: Issues and Ideas*, **2009**, *82*, 135-140.; Garcia-Ros, R.; Perez, F.; Talaya, I. *Electronic J. Res. Educ. Psych.* **2008**, *6*, 547-570.
3. Felder, R.M. Silverman, L.K. *Engr. Education*, **1988**, *78*, 674-681; Felder, R.M. *J. College Science Teaching*, **1993**, *23*, 286-290.; Lowery Bretz, S. *All Students are Not Created Equal: Learning Styles in the Chemistry Classroom*, Eds. Pienta, N. J., Cooper, M. M., Greenbowe, T. J. Chapter 3, in *Chemists' guide to effective teaching*, Pearson Education Inc., NJ, 2005.
4. Guest, S., Spence, C. *Intern. J. Psychophysiology*, **2003**, *50*, 63-80.
5. Chu S., Downes J. *Mem. Cognit.*, **2002**, *30*, 4, 511-518.
6. Gussarsky, E.; Gorodetsky, M. *J. Res. Sci. Teach.*, **1988**, *25*, 319-333.
7. Nakhleh, M. *J. Chem. Educ.* **1992**, *69*, 191-196.
8. Noh, T., Scharmann, L. C. *J. Res. Sci. Teach.* **1997**, *34*, 199-217.
9. Craig, E. R. R.; Kaufman, K. K. *J. Chem. Edu.* **1995**, *72*, A102.
10. Cooley, J. H., Williams, R. V. *J. Chem. Edu.* **1999**, *76*, 1117-1120.; Griswold, J.R.; Rauner, R. A. *J. Chem. Edu.* **1991**, *68*, 418-420.; Silvert, D. J. *J. Chem. Edu.* **1987**, *64*, 971-972.
11. Blackman, A. J. *J. Chem. Edu.* **1996**, *73*, 434-435.
12. Labuschagne, A. J. H.; Malherbe, J. S.; Meyer, C. J. *J. Chem. Edu.* **1994**, *71*, 1088-1090.
13. Herman, C. F. *J. Chem. Edu.* **1994**, *91*, 991-992.
14. Goller, W. J. Miller, J. H. *J. Chem. Edu.* **1993**, *70*, A159-160.
15. Uffelman, E. S.; Cox, E. H.; Goehring, J. B.; Lorig, T. S.; Davis, C. M. *J. Chem. Edu.* **2003**, *80*, 1368-1371.
16. *Chemistry of Scent: Structure of Smell*, Chemistry 1 Handbook, Lesson E37, University of Sidney, <http://firstyear.chem.usyd.edu.au/LabManual/E37.pdf>; (accessed February 2009).
17. Roderick, W. R. *J. Chem. Educ.* **1996**, *43*, 510-520.

18. Uchida, N.; Takahashi, Y. K.; Tanifuji, M.; Mori, K. *Nature Neuroscience* **2000**, *3*, 1035-1043.; Palmer, J. K. *J. Agric. Food Chem.*, **1973**, *21*, 923-925. *Small Molecules make Scents*, Science in Schools, Issue 6, <http://www.scienceinschool.org/2007/issue6/scents/>; (accessed February 2008).;
19. Savic, I. *Curr. Opin. Neurobiol.* **2002**, *12*, 455-461.
20. Good Scent Company, <http://www.thegoodscentcompany.com/>; (accessed January 2006).; Flavors & Fragrances, SAFC Supply Solutions Catalogs.
21. Shriner, R. L.; Herman, C. F.; Morrill, T. C.; Curtin, D. Y.; Fuson, R. C. *The Systematic Identification of Organic Compounds*, 8th ed.; John Wiley & Sons, Inc: New Jersey, 2004.
22. Solomons, T.W. Graham; Fryhle, Craig B. *Organic Chemistry*, 7th Ed., John Wiley and Sons, New York, 2000.; Bruckner, Reinhard. *Advanced Organic Chemistry: Reaction Mechanisms*, Harcourt Academic Press: San Diego, 2002.
23. Bromfield-Lee, D.C., Oliver-Hoyo, M. T. *J. Chem. Edu.* **2007**, *84*, 1976.
24. Doty, R. L.; Kerr, K. *Neuropsychologia*, **2005**, *43*, 1749-1753.; Doty, Richard L.; Applebaum, S., Zusho, H., Settle, R. G. *Neuropsychologia*. **1985**, *23*, 667-672.; Doty, R. L.; Psychophysical measurement of odor perception, In *The Human Sense of Smell*, Laing, D.G., Doty, R.L., Breipohl, W., Eds; Springer-Verlag: Berlin, 1992; pp 91-134.
25. O'Lenick Jr., A. J., Parkinson, J. K., *Journal of the Society of Cosmetic Chemists* **1994**, *45*, 247-256.
26. Liu, Y., Lotero, E., Goodwin, J. *Journal of Catalysis*, **2006**, *243*, 221-228.
27. Huang, Y., Sundmacher, K.; *Intern. J. Chem. Kin.* **2007**, *39*, 245-253.
28. Kolah, A., Asthana, N., Vu, D., Lira, C., Miller, D. *Indus. Eng. Chem. Res.* **2007**, *46*, 3180-3187.; McGoran, E. C.; Melton, C.; Taitch, D. *J. Chem. Edu.* **1996**, *73*, 88-89.
29. Gallaher, T., Gaul, D., Schreiner, S. *J. Chem. Edu.* **1996**, *73*, 465.; Hartel, A. M.; Hanna, J.M., Jr. *J. Chem. Edu.* **2009**, *86*, 475-476.
30. Puterbaugh, W. H.; Vanselow, C. H.; Nelson, K.; Shrawder, E. J. *J. Chem. Edu.* **1963**, *40*, 349-350.
31. Birney, D. M.; Starnes, S. D. *J. Chem. Edu.* **1999**, *76*, 1560-1561.
32. Williamson, K.L.; Little, J.G. *Microscale experiments for General Chemistry*, Houghton Mifflin Company, MA. 1997. pp 337-342.
33. Wade, P. A.; Rutkowsky, S. A.; King, D. B. *J. Chem. Edu.* **2006**, *83*, 927-928.; Hartel, Aaron M.; Hanna, James M., Jr. *J. Chem. Edu.* **2009**, *86*, 475-476.

34. *Making Scents: Synthesis of Esters*, Columbia University Department of Chemistry, <http://columbia.yosemite.cc.ca.us/ryanj/page1/page6/page41/page57/assets/scents.pdf>; (accessed May 2006).; *Esters*, Hartnell College; <http://www.hartnell.edu/faculty/showde/chem12b/esters.htm>; (accessed April 2007).; MHS Chemistry: Investigating Esters, <http://www.dbooth.net/mhs/chem/ester01.html>; (accessed June 2006).; *Synthesis of Methyl Benzoate by Fisher Esterification*, <http://courses.chem.psu.edu/chem36/Experiments/Exp84.pdf>; (accessed February 2009).; Clarke, M.; Brown, A.; Epp, D. N.; Gallup, M.; Wilson, J. R.; Wuerthele, J. A. *J. Chem. Edu.* **1986**, *63*, 1051-1052.
35. *Fischer Esterification: An ester from a carboxylic acid and an alcohol*, Experiment 10, CHEM360 Lab Manual 2002/04, [http://science.pc.athabascau.ca/chem360.nsf/f8ba9a4e31825f6f87256b6700619e85/\\$FILE/360Exp10-02.pdf](http://science.pc.athabascau.ca/chem360.nsf/f8ba9a4e31825f6f87256b6700619e85/$FILE/360Exp10-02.pdf); (accessed February 2009).; Wikholm, R. J. *Modular Laboratory Program in Chemistry: Preparation of Isopentyl Acetate by Fisher Esterification*, <http://www.cerlabs.com/experiments/10875407137.pdf>; (Accessed February 2009).
36. Holmes, L. H., Jr. *J. Chem. Edu.* **1991**, *68*, 501.
37. Pfennig, B.W.; Roberts, R.T. *J. Chem. Edu.* **2006**, *83*, 1804-1806.
38. Copper, C. L.; Koubek, E. *J. Chem. Edu.* **1999**, *76*, 1714-1715.
39. Schreck, J. O. *J. Chem. Edu.* **1966**, *43*, 149.
40. Takeoka, G.; Buttery, R.G.; Ling, L. *Food Sci. and Tech.* **1996**, *52*, 677-680; Takeoka, G.; Buttery, R.G.; Turnbaugh, J.G.; Benson, M. *Food Sci. and Tech.* **1995**, *28*, 153-156; Salo, P.; Nykänen, L.; Suomalainen, H. *J. Food Sci.* **1972**, *37*, 394-398; Measurement of Odor Threshold by Triangle Odor Bag Method. http://www.env.go.jp/en/air/odor/measure/02_3_2.pdf (Last accessed December 7th, 2007); Sigma-Adrich MSDS online. www.sigmaaldrich.com (Last accessed 15th January, 2008). Liu, Y.; Lotero, E.; Goodwin, J. *J. Catal.*, **2006**, *243*, 221-228.; Buttery, R.G.; Ling, L.; Guadagni, D.G. *J. Agr. Food Chem.* **1969**, *17*, 385-389.; Takeoka, G. R.; Flath, R.A.; Mon, T. R.; Teranishi, R.; Guentert, M. *J. Agric. Food Chem.* **1990**, *38*, 471-477. Sigma-Adrich MSDS online. www.sigmaaldrich.com (Last accessed 15th January, 2008).
41. Vollhardt, K.P.C.; Schore, N.E. *Organic Chemistry*, 2nd edition, W.H. Freeman and Company, New York, **1994**, page 739.
42. Bromfield-Lee, D. C.; Oliver-Hoyo, M. T. *J. Chem. Edu.* **2009**, *86*, 82-84.
43. Worrell, J. H. *LabTrek: Experiments for General Chemistry*, 3rd ed., Contemporary Publishing Co., NC, 1997; pp 333-344; Aukszi, B. *General Chemistry 2 Laboratory*, 2nd ed., Outernet Publishing, LLC, MN, 2004; 73-82.; Levine, S. L. *Laboratory Manual for Chemistry 102*, Pearson Custom Publishing, 2002; Chapter V: Reaction Energetics and Chemical Reactions, pp 13-25.
44. DeMeo, S. *J. Chem. Edu.* **2002**, *79*, 474-475.
45. Van Driel, J. H.; de Vos, W.; Verloop, N. *J. Chem. Edu.* **1999**, *76*, 559-561.; Grant, A. W., Jr. *J. Chem. Edu.* **1984**, *61*, 466.

46. Barrera, N. M.; McCarty, J. L.; Dragojlovic, V. *Chem. Educator*, **2002**, 7, 142-145.
47. Anderson, M.; Buckley, A. *J. Chem. Edu.* **1996**, 73, 639-640.
48. Stolzberg, R. J. *J. Chem. Edu.* **1999**, 76, 640-641.
49. Rudd, J. A., II; Greenbowe, T. J.; Hand, B. M.; *J. Chem. Edu.* **2007**, 84, 2007-2011.
50. Tyson, L.; Treagust, D. F.; Bucat, R. B. *J. Chem. Edu.* **1999**, 76, 554-558.
51. Canpolat, N.; Pinarbasi, T.; Bayrakceken, S.; Geban, O. *Res. Sci. Tech. Educ.* **2006**, 24, 217-235.
52. Chiu, M.H.; Chou, C.C.; Liu, C. J. *J. Res. Sci. Teach.*, **2002**, 39, 688-712.
53. Chang, R. *Chemistry*, 5th Ed. McGraw-Hill Inc., NJ, **1994**, 53-678.; Wertz, D. W. *Chemistry: A molecular Science*, 2nd edition, Pearson Custom printing, 2006, 208-214, 238-239.; Solomons, T.W. Graham; Fryhle, Craig B. *Organic Chemistry*, 7th Ed., John Wiley and Sons, New York, 2000. 828-883.; Kotz, J. C.; Treichel, P. Jr. *Chemistry and Reactivity*, 3rd Ed. Saunders College Publishing, 1996. 749-793.
54. *Chemical Equilibrium labs*: <http://phs.prs.k12.nj.us/rcorell/EquilibriumLab.pdf>; <http://chemistry.olivet.edu/classes/chem100/pdf/Labs/Equilibrium%20Lab.PDF>; (last accessed February 2009).; *Spectrophotometric Determination of an Equilibrium Constant*, <http://www2.bc.edu/~oconnell/Gen%271/Equilibrium.pdf>; (last accessed September 2006).; *Le Chatelier's principle*; <http://www.chemguide.co.uk/physical/equilibria/lechatelier.html>; (accessed July 2006).
55. Sample data: Brito,F.; Ascanio,J.; Mateo,S.; Hernández,C.; Araujo,L.; Gili,P.; Martín-Zarza,P.; Domínguez,S.; Mederos,A. *Polyhedron*, **1997**, 16, 3835-3846.; CRC Handbook of Chemistry and Physics, Section 5, 89th Ed., Taylor and Francis LLC, 2009.; So, M. P. Oh, Y. *Bull. Korean Chem. Soc.* **1982**, 3, 5-9.; Reichlek, R. A.; M^cCurdy, K. G.; Hepler, L. *Can. J. Chem.* **1975**, 53, 3841-3845.; Zhang, Y.; Muhammed, M. *Hydrometallurgy*, 2001, **60**, 215-236., Stina Bergström, N.; Olofsson, G. *J. Sol. Chem.* **1978**, 7, 497-513.; Miller, J.G., Lowell, A. I.; Lucasse, W. W. *J. Chem. Soc.* **1947**, 121-128.; Richards, T. W., Mair, B. J. *J. Am. Chem. Soc.*, **1929**, 51, 737-740.; Kegeles, G. *J. Am. Chem. Soc.*, **1940**, 62, 3230-3232.; Ellinson, E. O. *J. Am. Chem. Soc.*, **1915**, 37, 699-709.
56. Taube, H., *Chem. Rev.* 1952 50, 69-126.
57. Irving, H.M.N.H; Williams, R.J.P. *J. Chem. Soc.* **1953**, 3192-3210.
58. CRC Handbook of Chemistry and Physics, Section 8, 89th Ed., Taylor and Francis LLC, 2009.
59. Drying Organic Solutions, <http://orgchem.colorado.edu/hndbksupport/drying/drying.html>, (accessed May 2007).; Drying agents, <http://www.chem.ucalgary.ca/courses/351/laboratory/drying%20agents.pdf>, (accessed March 2009).; Burfield, D. R.; Lee, K.; Smithers, R. H. *J. Org. Chem.* **1977**, 42, 3060-3065.

60. Johnstone, A. H.; MacDonald, J.J; Webb, G. *Educ. in Chem.* **1977**, *14*, 169-171.
61. Bilgin, I. *Inter. J. Sci. Math. Educ.*, 2006, *4*, 467-484.
62. Gorodetsky, M.; Gussarsky, E. *Eur. J. Sci. Educ.*, **1986**, *8*, 427-441.
63. Mathabatha, S. S. Dissertation: The effect of laboratory based teaching and traditional based teaching on students' conceptual understanding of chemical equilibrium. University of Pretoria, South Africa, 2005.
64. Chiu, M., Chou, C., Liu, C. *J. Res. Sci. Teach.*, **2002**, *39*, 688-712.
65. Bergquist, W., Heikkinen, H. *J. Chem. Edu.* **1990**, *67*, 1000.
66. Tyson, L., Treagust, D. F., Bucat, R. B. *J. Chem. Edu.* **1999**, *76*, 554.
67. Hackling, W.M.; Garnett, J.P. *Eur. J. Sci. Educ.* **1985**, *7*, 205-214.
68. Huddle, P.A.; Ncube, C. *Spectrum*, **1994**, *32*, 39-40.; Huddle, P. A.; White, M. D.; Rogers, F. *J. Chem. Edu.* **2000**, *77*, 920.
69. Allen, D. A. **2005**, The Development and Assessment of an Active Learning environment: cAcL2, concept Advancement through chemistry Laboratory-Lecture. PhD thesis, NCSU.
70. Battino, R. *J. Chem. Edu.* **1975**, *52*, 55.
71. Bartholow, M. *J. Chem. Edu.* **2006** *83*, 48A.; Hanson, R. M. *J. Chem. Edu.* **2003**, *80*, 1271.; Edmonson, L. J., Lewis, D. L. *J. Chem. Edu.* **1999**, *76*, 502.
72. Wilson, A. H. *J. Chem. Edu.* **1998**, *75*, 1176.
73. Sariçayır, H.; Şahin, M., Üce, M. *Eurasia J. Math. Sci. & Tech. Ed.*, **2006**, *2*, 130-137.
74. Wheeler, A.E.; Kass, H. *Sci. Educ.*, **1978**, *62*, 223-232.; Wheeler, A.E.; Kass, H. *Students Misconceptions in Chemical Equilibrium as Related to Cognitive Level and Achievement*, Paper presented at the annual NARST Meeting., Illinois, 1974.
75. Gupta, Y.K. *J. Indian Chem. Soc.* **2007**, *84*, 792-800.
76. Sullivan, J.H. *J. Chem. Phys.* **1969**, *51*, 2288.
77. Horiuti, J. *Z. Phys. Chem. Neue. Fol.* **1957**, *12*, 321-323.; Manes, M., Hofer, L. J. E., Weller, S. *J. Chem. Phys.* **1950**, *18*, 1355.
78. Chang, R. *Chemistry*, 5th Ed. McGraw-Hill Inc., NJ, **1994**, pg 564-589.
79. Devoe, H. *Thermodynamics and Chemistry*, Prentice Hall, NJ, **2001**; pg 279-298.

80. Hansen, R. C.; Krause, P. F. *J. Chem. Edu.* **1984**, *61*, 804.
81. Banerjee, A. C. *J. Chem. Edu.* **1995**, *72*, 879.
82. Canagaratna, S. G. *J. Chem. Edu.* **2003**, *80*, 1211.; Harris, W. F. *J. Chem. Edu.* **1982**, *59*, 1034.
83. Carl, D. W. *J. Chem. Edu.* **1988**, *65*, 407.; Torres, E. M. *J. Chem. Edu.* **2007**, *84*, 516.
84. Pedrosa, M. A.; Dias, M. H. *Chem. Edu. Res. Prac. Eur.* **2000**, *1*, 227-236.
85. Stavridou, H., Solomonidou, C. *Int. J. Sci. Ed.* **1989**, *11*, 83-92.
86. Raviolo, A. *J. Chem. Edu.* **2001**, *78*, 629.
87. Steffel, M. J. *J. Chem. Edu.* **2006**, *83*, 1185.; Chang, R. *Chemistry*, 5th Ed. McGraw-Hill Inc., NJ, **1994**; pg 564-589.
88. Gussarsky, E.; Gorodetsky, M. *J. Res. Sci. Teach.*, **1990**, *27*, 197-204.; Gussarsky, E.; Gorodetsky, M. *J. Res. Sci. Teach.*, **1988**, *25*, 319-333.
89. Huddle, P.A.; Pillay, A.E. *J. Res. Sci. Teach.* **1996**, *33*, 65-77.
90. Caldwell, W. E. *J. Chem. Edu.* **1932**, *9*, 2079.; Garritz, A. *J. Chem. Edu.* **1997**, *74*, 544.; Olney, D. J. *J. Chem. Edu.* **1988**, *65*, 696.
91. Gage, B. A. **1986**, *Quantitative aspects of equilibrium systems*. PhD thesis, University of Maryland, College Park.
92. Banerjee, A. C. *Int. J. Sci. Educ.* **1991**, *13*, 487-494.
93. Bapoo, A. H.; Bradley, J. D.; Gerrans, G. C. *Spectrum* (Pretoria, South Africa), **1992**, *30*, 10-12.
94. Bapoo, A. H.; Bradley, J. D.; Gerrans, G. C. *Spectrum* (Pretoria, South Africa), **1992**, *30*, 52-53.
94. Harris, W. F. *J. Chem. Edu.* **1982**, *59*, 1034.
95. Solaz-Portolés, J. J.; Quílez, J. *J. Res. Sci. Teach.* **1995**, *32*, 939-957. Solaz-Portolés, J. J., Quílez-Pardo, J. *Revista Mexicana de Física*, **1995**, *41*, 128-138.; Solaz-Portolés, J. J.; Quílez, J. *Chem. Educ.: Res. Pract. Eur.*, **2001**, *3*, 303-312.
96. Huddle, P.A. *J. Chem. Edu.* **1998**, *75*, 1175.
97. Mahan, B. *J. Chem. Edu.* **1963**, *40*, 293.
98. Cheung, D. *J. Chem. Edu.* **2009**, *86*, 514-518.
99. Brice, L.K. *J. Chem. Edu.* **1983**, *60*, 387.

100. Bradley, J. D.; Gerrans, G. C.; Long, G.C. *Spectrum* (Pretoria, South Africa), **1989**, 27, 13-15.
Bradley, J. D.; Gerrans, G. C.; Long, G.C. *Spectrum* (Pretoria, South Africa), **1989**, 27, 9-10.
101. Taber, K. S. Chemical misconceptions - prevention, diagnosis and cure, L: Volume 2: classroom resources, London: Royal Society of Chemistry, 2002.
102. Marrs, P. S. *J. Chem. Edu.* **2004**, 81, 870., Fernandez, L. T. H.; Klappmeier, F. H. *J. Chem. Edu.* **1978**, 55, 266.; Catalysis: The pH-Rate Dependence of the Hydrolysis of Aspirin, Organic Chem 465, Experiment 35; <http://web.uvic.ca/~pmarrs/chem465/465e35aspirinhydrolysis.pdf>; (accessed February 2009). Kinetics of Aspirin Degradation in Aqueous Solution, Physical Chemistry 526; www.pharmacy.umaryland.edu/faculty/ghollenb/pchem/lab2/asa%20lab.doc; (access February 2009).; Chourhury, S.; Mitra, A. K. *Pharm. Research*, **1993**, 10, 156-159.; Garnett, E.R. *J. Am. Chem. Soc.*, **1957**, 79, 3401-3408.
103. Borer, L. L., Barry, E. *J. Chem. Edu.* **2000**, 77, 354-355., Street, K.W. Jr. *J. Chem. Edu.* **1988**, 65, 914.; Williamson, K.L.; Little, J.G. *Microscale experiments for General Chemistry*, Houghton Mifflin Company, MA. 1997. pp 329-333.
104. Solomon, S.; Hur, C.; Lee, A.; Smith, K. *J. Chem. Edu.* **1996**, 73, 173-174.; Fersht, A. R.; Kirby, A. J. *J. Am. Chem. Soc.*, **1967**, 89, 4857-4863.
105. Sample sources: Worrell, J. H.; *LabTrek, Experiments for General Chemistry*, 3rd Ed., Contemporary Publishing Co., Raleigh, NC, **1997**.; Williamson, K.L.; Little, J.G. *Microscale experiments for General Chemistry*, Houghton Mifflin Company, MA. 1997.; Aukszi, B. *General Chemistry 2 Laboratory*, 2nd ed., Outernet Publishing, LLC, MN, 2004.; Levine, S. L. *Laboratory Manual for Chemistry 102*, Pearson Custom Publishing, 2002; Chapter.; Blackman, D. *J. Chem. Edu.* **1978**, 55, 722-723.; Derek, J. *J. Chem. Edu.* **1966**, 43, 34-35.; Chebolu, V.; Storandt, B. C. *J. Chem. Edu.* **2003**, 80, 305-306.
106. BouJaoude, S. Students' Systematic Errors When Solving Kinetic and Chemical Equilibrium Problems., Paper presented at the Annual Meeting of the National Association for Research in Science Teaching (Atlanta, GA, April 16-19, 1993).; Novak, I. *J. Chem. Educ.* **1998**, 75, 1574-1575.
107. Lee, J. *J. Chem. Edu.* **2008**, 85, 141-144.
108. Reeve, J. C. *J. Chem. Edu.* **1991**, 68, 728.
109. Quisenberry, K. T., Tellinghuisen, J. *J. Chem. Edu.* **2006** 83, 510-512.
110. Mason, T. J., Lorimer, J. P., Bull, P. H. *Educ.Chem.*, **1985**, 22, 110-112.
111. Laidler, K. J., Glasstone, S. *J. Chem. Edu.* **1948**, 25, 383.
112. Last, A. M. *J. Chem. Edu.* **1983**, 60, 748., Last, A. M. *J. Chem. Edu.* **1985**, 62, 1015.
113. Fortman, J. J. *J. Chem. Edu.* **1994**, 71, 848-849.
114. Evenson, Andy. *J. Chem. Edu.* **2002**, 79 822-823.

115. Olbris, D. J.; Herzfeld, J. *J. Chem. Edu.* **2002**, *79* 1232.; Schultz, E. *J. Chem. Edu.* **1997**, *74* 505.; Castillo, R. *The Physics Teacher*, **1968**, *6*, 467–468.
116. Logan, S. R. *Educ. Chem.* **1984**, *21*, 20-21.
117. DePierro, Ed; Garafalo, Fred; Toomey, Rick T. *J. Chem. Edu.* **2008**, *85*, 1226.
118. Sanger, M. J., Wiley, R. A., Jr., Richter, E. W., Phelps, A. J. *J. Chem. Edu.* **2002**, *79*, 989-991.
119. Bradley, J. D.; Brand, M. *J. Chem. Edu.* **1985**, *62*, 318.
120. Johnstone, A. H. *J. Chem. Edu.* **1993**, *70*, 701.
121. Gabel, D. L., Samuel, K. V., Hunn, D. *J. Chem. Edu.* **1987**, *64*, 695-697. Gabel, D. L. *J. Chem. Edu.* **1993**, *70*, 193-194.; Gabel, D. L., Briner, D., Haines, D. *Sci. Teacher*, **1992**, *59*, 58-63.
122. Selvaratnam, M. *S. African J. Chem.* **1998**, *51*, 2.
123. Griffiths, A., Preston, K. *J. Res. in Sci. Teaching* **1992**, *29*, 611–628.
124. Smith, K. J., Metz, P. A. *J. Chem. Educ.* **1996**, *73*, 233-235.
125. Arasasingham, R. D., Taagepera, M., Potter, F., Lonjers, S. *J. Chem. Edu.* **2004**, *81*, 1517-1522.; Arasasingham, R. D., Taagepera, M., Potter, F., Martorell, I., Lonjers, S. *J. Chem. Edu.* **2005**, *82*, 1251-1262.
126. Crawshaw, J., Chambers, J. A Concise course in A-Level Statistics with Worked Examples. Pages **1994**, 635-643. The Bath press, Great Britain.
127. G. A. Vaughan; *Thermometric and enthalpimetric titrimetry*; Van Nostrand Reinhold Company: London, 1973.; Barthel, J. *Thermometric titrations*; Chemical Analysis, A Series of Monographs on Analytical chemistry and it's Applications, Volume 45; John Wiley & Sons: New York, 1975.; Tyrrell, H. J. V., Beezer, A. E. *Thermometric Titrimetry*, Chapman and Hall Ltd, London, 1968.
128. Williams, D.R. *Educ. Chem.*, **1971**, *8*, 97-99.
129. Smith, R. L.; Popham, R. E. *J. Chem. Edu.* **1983**, *60*, 1076-1077.
130. Hansen, L. D.; Kenney, D.; Litchman, W. M., Lewis, E. A.; *J. Chem. Edu.* **1971**, *48*, 851.
131. *Thermometric Titration of Pyridine*,
<http://www.colby.edu/chemistry/PCChem/lab/Thermometricpyridine.pdf>, (accessed April 2009).
132. *Practical Chemistry: A thermometric titration*,
<http://www.practicalchemistry.org/experiments/a-thermometric-titration,279,EX.html>, (accessed April 2009).

133. Worrell, J. H.; *LabTrek, Experiments for General Chemistry*, 3rd Ed., Contemporary Publishing Co., Raleigh, NC, **1997**; pp 355-379.
134. Copper, C. L.; Koubek, E. *J. Chem. Edu.* **2001**, *78*, 652.; Silva, C. R.; Simoni, J. A.; Collins, C. H.; Volpe, P. L. O. *J. Chem. Edu.* **1999**, *76*, 1421.; Worrell, J. H.; *LabTrek, Experiments for General Chemistry*, 3rd Ed., Contemporary Publishing Co., Raleigh, NC, **1997**; pp 167-175.; Williamson, K.L.; Little, J.G. *Microscale experiments for General Chemistry*, Houghton Mifflin Company, MA. 1997. pp 157-173.
135. Richardson, J. N.; Stauffer, M. T.; Henry, J. L. *J. Chem. Edu.* **2003**, *80*, 65-67.
136. Sowa, S.; Kondo, A. E. *J. Chem. Edu.* **2003**, *80*, 550-551.; Rogers, C. U. *J. Chem. Edu.* **1969**, *A34*.; Alyea, H. N. *J. Chem. Edu.* **1969**, *A634*.
137. Flint, E. B.; Kortz, C. L.; Taylor, M. A. *J. Chem. Edu.* **2002**, *79*, 705-705.
138. Ma, N. L.; Tsang, C. W. *J. Chem. Edu.* **1998**, *75*, 122.; Barreto, M. S.; Medeiros, L.; Furtado, P. *J. Chem. Edu.* **2001**, *78*, 91-92.
139. Papadopoulos, N.; Limniou, M. *J. Chem. Edu.* **2003**, *80*, 709.; Aukszi, B. *General Chemistry 2 Laboratory*, 2nd ed., Hayden McNeil Publishing, Inc, MI, 2003; 87-100.
140. Barcza, L.; Buvári-Barcza, Á. *J. Chem. Edu.* **2003**, *80*, 822-828.
141. Kraft, A. *J. Chem. Edu.* **2003**, *80*, 554-559.
142. Castillo S. C.; Micolta S. G.; Grajales T. M. *J. Chem. Edu.* **1984**, *61*, 1067-1068.
143. Deal, S. T.; Pope, S. R. *J. Chem. Edu.* **1996**, *73*, 547.
144. Worrell, J. H.; *LabTrek, Experiments for General Chemistry*, 3rd Ed., Contemporary Publishing Co., Raleigh, NC, **1997**; pp 177-189.; Williamson, K.L.; Little, J.G. *Microscale experiments for General Chemistry*, Houghton Mifflin Company, MA. 1997. pp 157-164.
145. Burgstahler, A. W.; Bricker, C. E. *J. Chem. Edu.* **1991**, *68*, 332-333.
146. Marzacco, C. J. *J. Chem. Edu.* **1999**, *76*, 1517.
147. Diogo, H. P.; Minas da Piedade, M. E.; Moura Ramos, J. J.; Sirnoni, J. A.; Martinho Simoes, J. A. *J. Chem. Educ.* **1992**, *69*, 940-942.; Kavanagh, E.; Mindel, S.; Robertson, G.; Hughes, D. E. P. *J. Chem. Edu.* **2008**, *85*, 1129-1130.; Wadsö, L.; Smith, A. L.; Shirazi, H.; Mulligan, S. R.; Hofelich, T. *J. Chem. Edu.* **2001**, *78*, 1080-1086.; Bartle, K. D.; Osborn, P. M. *J. Chem. Edu.* **1973**, *50*, 637.
148. Mills, K. V.; Guilmette, L. W. *J. Chem. Edu.* **2007**, *84*, 326-328.
149. Mahoney, D. W.; Sweeney, J. A.; Davenport, D. A.; Ramette, R. W. *J. Chem. Edu.* **1981**, *58*, 730-731.; Hayes, S. E. *J. Chem. Edu.* **1995**, *72*, 1029-1031.

150. de Vos, W.; Verdonk, A. H. *J. Chem. Edu.* **1986**, *63*, 972-974.
151. Nakhleh, M., Krajcik, J.S. *J. Res. Sci. Teach.* **1994**, *30*, 1149-1168.; Nakhleh, M., Krajcik, J.S. *J. Res. Sci. Teach.* **1993**, *31*, 1077-1096.
152. Sheppard, K. *Chem. Educ. Res. Prac.* **2006**, *7*, 32-45.
153. Furió-Más, C.s; Calatayud, M.; Bárcenas, S. L. *J. Chem. Edu.* **2007**, *84*, 1717-1724.
154. Garin, D. L., *J. Chem. Edu.* **1968**, *45*, 37.; Kavanagh, E.; Mindel, S.; Robertson, G.; Hughes, D. E. P. *J. Chem. Edu.* **2008**, *85*, 1129-1130.; Schneider, T.; Politi, M. J.; Baptista, M. S. *J. Chem. Edu.* **2002**, *79*, 503-505.; Wadsö, L.; Smith, A. L.; Shirazi, H.; Mulligan, S. R.; Hofelich, T.. *J. Chem. Edu.* **2001**, *78*, 1080-1086.
155. Canagaratna, S. B., Witt, J. *J. Chem. Edu.* **1998**, *65*, 126-129.
156. Keily, H. J., Hume, D. N. *Anal. Chem.*; **1956**, *28*, 1294 – 1297.
157. Bender, P., Biermann, W.J. *J. Am. Chem. Soc.* **1952**, *74*, 684-707.; Bierman, W. J. *Can. J. Chem.*, 1960, *38*, 57-60.
158. Bell, J. M.; Cowell, C F. *J. Am. Chem. Soc.*; **1913**, *35*, 49 – 54.; Joseph Jordan, J.; Dumbaugh Jr., H. *Anal. Chem.*; **1959**, *31*, 210 - 213;
159. Kegeles, G. *J. Am. Chem. Soc.* **1940**, *62*, 3230,-3232.
160. Parry-Jones, R. L. *Education in Chemistry*, **1976**, *13*, 76-77.
161. *Concentrative Properties of Aqueous Solutions: Density, Refractive Index, Freezing Point Depression, and Viscosity*, CRC Handbook of Chemistry and Physics, 89th Ed., Section 8, Taylor and Francis LLC, 2009.; Source: MSDS data; Density Tables, http://www.chembuddy.com/?left=CASC&right=density_tables, (accessed February 2009).
162. Papee, H. et.al, *Can. J. Chem.* **1956**, *34*, 1677-1682.
163. Enthalpy of Dilution of Acids, CRC Handbook of Chemistry and Physics, Section 5, 89th Ed., Taylor and Francis LLC, 2009.
164. Richards, T. W.; Mair, B. J. *J. Amer. Chem. Soc.* **1929**, *51* (3), 737-740.
165. Burt, N. E. *J. Chem. Edu.* **1973**, A178.; Hambly, A. N. *J. Chem. Edu.* **1969**, A55.; Endothermic Reaction, <http://jchemed.chem.wisc.edu/jcesoft/cca/CCA3/MAIN/ENDO2/PAGE1.HTM>, (accessed May 2007).
166. Schmidt, H. *Sci. Edu.* **1997**, *81*, 123-135.
167. Schmidt, H. *Int. J. Sci. Edu.* **1991**, *13*, 459-471.

168. Demircioğlu, G., Ayas, A., Demircioğlu, H. *Chem. Educ. Res. Pract.*, **2005**, 6, 36-51.
169. Nakhleh, M. *J. Chem. Edu.* **1994**, 71, 495-499.
170. Cros, D., Chastrette, M., Fayol, M. *Intern. J. Sci. Educ.*, **1988**, 10, 331; Cos, D., Maurin, M., Amouroux, R., Chastrette, M., Weber, J., Fayol, M. *Eur. J. Sci. Edu.*, **1986**, 8, 305-313.
171. Ross, B., Munby, H. *Intern. J. Sci. Educ.*, **1991**, 13, 11.
172. De Jong, O., Acampo, J., Verdonk, A. *J. Res. Sci. Teach.* **1995**, 31, 1097-1110.; Gilbert, J. *Chemical Education: Towards-Research Based Practice*, Chapter 14, De Jong, O. Treagust, D. **2002**, Boston Kluwer Academic Publishers.
173. Bradley, J.D.; Mosimege, M.D. *S. Afr. J. Chem.*, **1998**, 51, 137-145.
174. Garnett, P. J., Treagust, D. F. *J. Res. Sci. Teach.* **1992**, 29, 1079-1099; Garnett, P. J., Treagust, D. F. *J. Res. Sci. Teach.* **1992**, 29, 121-142.
175. Parkin, G. *J. Chem. Edu.* **2006**, 83, 791.; Smith, D. W. *J. Chem. Edu.* **2005**, 82, 1202.
176. Herron, J.D. *J. Chem. Edu.* **1975**, 51-52.
177. Cox, A. L., Cox, J. R. *J. Chem. Edu.* **2002**, 79, 965.
178. Chang, R. *Chemistry*, 5th Ed. McGraw-Hill Inc., NJ, **1994**, pg 100-119.; Wertz, D. W. *Chemistry: A molecular Science*, 2nd edition, Pearson Custom printing, 2006, D365-368.
179. Wertz, D. W. *Chemistry, A Molecular Science*, 2006, 2nd Edition, Prentice Hall, 247-259.
180. Niaz, M. *J. Sci. Edu. Tech.* **2006**, 15, 269-276.
181. Thomaz, M. F., Malaquias, I. M., Valente, M. C., Antunes, M. J. *Physics Education*, **1995**, 30, 19-26.
182. Greenbowe, T. J., Meltzer, G. E. *Int. J. Sci. Edu.* **2003**, 25, 779-800.
183. Barrow, G. M. *J. Chem. Edu.* **1988**, 65, 122-125.
184. Chang, R. *Chemistry*, 5th Ed. McGraw-Hill Inc., NJ, **1994**, pg 207-228.
185. Beall, H. *J. Chem. Edu.* **1994**, 71, 1056.
186. Vincent, A. *Educ. in Chem.*, **1981**, 18, 114-15.
187. Huddle, P.A.; Pillay, A.E. *J. Res. Sci. Teach.* **1996**, 33, 65-77.
188. Frazer, M. J.; Servant, D. *Educ. in Chem.* **1986**, 23, 54-56.; Selvaratnam, M.; Canagaratna, S. *G. J. Chem. Edu.* **2008**, 85, 381.

189. Ault, A. *J. Chem. Edu.* **2001**, 78, 1347.; Watkins, S. F. *J. Chem. Edu.* **2003** 80 658.; Tyndall, J.R. **1975**, 52, 492.
190. Nakhleh, M. *J. Chem. Edu.* **1994**, 71, 495-499.
191. Zoller, U. *J. Chem. Edu.* **1993**, 70, 195.
192. Carlton, T. S. *J. Chem. Edu.* **1997**, 74, 939-941.
193. Dauvergne, X., Ce'rantola, S., Salaün, S., Magne', C., Kervarec, N., Bessièresa, M., Deslandesa, E. *Carbohydrate Research*, **2006**, 341, 2166–2169.
194. Fenwick, G. E., Heaney, R. K. *Food Chemistry*, **1983**, 11, 249-271.
195. Carlson, D. G.; Daxenbichler, M. E.; VanEtten, C. H.; Tookey, H. L.; Williams, P. H. *J. Agric. Food. Chem.* **1981**, 29, 1235-1239., Hopkins, R. J., Griffiths, D. W. , E. Birch, A. N. *J. Chemical Ecology*, **1998**, 12, 2003-2019.
196. Truscott, R. J., Johnstone, P. K., Minchinton, I. R., Sang, J. P. *J. Agric. Food Chem.* **1983**, 31, 863-867.
197. Hing, F.S., Weckel, K.G. *J. Food Sci.* **1964**, 29: 149-157.
198. Mullin, W. J., Sahasrabudhe, M. R. *Can. Inst. Food Sci. Technol. J.*, **1978**, 11, 50-52.
199. Barillari, J., Cervellati, R., Paolini, M., Tatibouët, A., Rollin, P., Iori, R. *J. Agric. Food Chem.* **2005**, 53, 9890-9896.
200. Uda, Y., Kurata, T., Arakawa, N. *Agric. Biol Chem.*, **1986**, 50, 2741-2746.
201. Botti, M.G., Taylor, M. G., Botting, N. P. *J. Biological Chem.* **1995**, 270, 20530-20535.
202. Björkman, R.; Lönnerdal, B. *Biochimica et Biophysica Acta.* **1973**, 327, 121-131.
203. Clayton C. J., Hughes, N. A., Saeed, S. A. *J. Chem. Soc. C*, **1967**, 644-648.; Satchell, D. P. N., Satchell, R. S. *Chem. Soc. Rev.*, **1990**, 19, 55-81.
204. Lartey, P.A., Fredor, L. *Carbohydrate Research*, **1979**, 69, 89-95.
205. Fife, T.H.; Jao, L. K. *J. Am. Chem. Soc.*, **1969**, 91, 4217-20.
206. Fife, T. H., Anderson, E. *J. Am. Chem. Soc.*, **1970**, 92, 5464-5468.
207. Bamford, C. Capon, B., Overend., W. G. *J. Chem. Soc.* **1962**, 5138-5141.
208. Pihlaja, K. *J. Am. Chem. Soc.*, **1972**, 94, 3330-3334.
209. De, N. C., Fedor, L. R. *J. Am. Chem. Soc.*, **1968**, 90, 7266-7271.

210. Jensen, J. L., Jencks, W. P. *J. Am. Chem. Soc.*, **1979**, 101, 1476-1488.
211. Bones, A. M., Rossiter, J. T. *Phytochemistry*,
212. Li, J. J. *Name Reactions: a collection of detailed reaction mechanisms*, 3rd ed., page 352, Published, London; 2006.
213. Fenwick, G. E., Heaney, R. K. *Food Chemistry*, **1983**, 11, 249-271.
214. Gronowitz, S., Svensson, L., Ohlson, R. *J. Agric. Food Chem.* **1978**, 26, 887-890.
215. Smolinska, U.; Morra, M. J.; Knudsen, G. R.; Brown, P. D. *Phytopathology*. **1997**, 87, 77-82.
216. Das, S.; Tyagi, A. K.; Kaur, H. *Current Science*, **2000**, 79, 1665-1671.; Higdon, J.V.; Delage, B.; Williams, D. E.; Dashwood, R. H. *Pharmacological Research*, **2007**, 55, 224-236.
217. Truscott, R. J. W., Manthey, M. K. *J. Sci. Food Agri.* **1989**, 47, 191-195.
218. Ishii, H.; Hanaoka, T.; Asaka, T.; Harada, Y.; Ikeda, N. *Tetrahedron*, **1976**, 32, 2693-2698.; Zimmer, H.; Lankin, D. C.; Horgan, S. W. *Chem. Rev.*, **1971**, 71, 229-246.; Remers, W. A.; Weiss, M. J. *J. Am. Chem. Soc.*, **1966**, 88, 804-813.
219. Barillari, J.; Canistro, D.; Paolini, M.; Ferroni, F.; Pedulli, G. F.; Iori, R.; Valgimigli, L. *J. Agric. Food Chem.* **2005**, 53, 2475-2482.; Barillari, J.; Iori, R.; Broccoli, M.; Pozzetti, L.; Canistro, D.; Sapone, A.; Bonamassa, B.; Biagi, G. L.; Paolini, M. *Agric. Food Chem.* **2007**, 55, 5505-5511.
220. Khalifa, N.; Ramla, M.; Amr, Abd E.; Abdulla, M. Phosphorus, Sulfur, and Silicon and the Related Elements, **2008**, 183, 3046-3062.
221. S. B. Baker, *J. Amer. Chem. Soc.* **1952**, 74, 827-828.
222. Pottenger, C. R.; The mechanism of cerium (IV) oxidation of glucose and cellulose, Dissertation, Georgia Institute of Technology, 1968 Publisher, <http://hdl.handle.net/1853/5522>, (accessed March 2009).
223. Evans, W. L.; Buehler, C. A.; Looker, C. D.; Crawford, R. A.; Holl, C. W. *J. Am. Chem. Soc.*, **1925**, 47, 3085-3098.
224. Merbouh, N.; Bobbit, J. M.; Brückner, C. *Tetrahedron Letters*, **2001**, 42, 8793-8796.
225. Kuramshinl, E. M.; Ulakm, O. K.; Nazarovs, N.; Zlotsky, S.; Rakhmankulov, D. L. *Journal für Praktische Chemie*, **1989**, 331, 591-599.
226. Napolitano, A.; D'Ischia, M.; Prota, G.; Schultz, T. M.; Wolfram, L. J. *Tetrahedron*, **1989**, 45, 6749-60.; Goyal, R. N.; Kumar, N. *Bioorganic Chemistry*, **1999**, 27, 239-252.

CHAPTER 4 . Conclusions and Future Work

4.1 Summary and Conclusions

Chemistry experiments typically investigate chemical concepts exclusively through the sense of sight. An examination of the literature (Section 1.2) showed few experiments published which utilize multiple senses in the teaching laboratory. Some of the experiments reviewed include the sense of smell for olfactory titrations (1), observation of sound using buzzers rather than LED lights to test conductivity (2), and haptic technology using the sense of touch to explore molecular structures (3). The sensory processes, perceptual processes and sensory thresholds were reviewed in order to demonstrate the usefulness of the senses in making chemical determinations (Section 1.3). Multi-sensory learning benefits *all* students by actively engaging them in learning and provides increased exposure to the material through multiple senses thus increasing attention towards the concepts (Section 1.4). Several chemistry experiments that rely on different senses to investigate chemical concepts, make quantitative determinations, and familiarize students with chemical techniques traditionally done using only the sense of sight were developed and implemented into the undergraduate laboratory (Chapter 3).

The research objectives of this project were both chemical and pedagogical in nature. These objectives were successfully incorporated into the sensorial experiments as discussed in Chapter 2. Objectives specific to each experiment were also addressed in Chapter 3.

Chemical: The chemical goals and considerations of this project for each experiment were:

- i) Manipulation of chemical reactions or utilization of non-traditional observations to allow for exploration of chemical principles via sensorial changes.
- ii) Evaluation of chemical hazards, properties and suitability for the teaching laboratory.
- iii) Consideration of adoption measures and accessibility of materials.

iv) Rigorous testing for the determination of data accuracy.

i) Multi-sensory observations. Experiments chosen were conceptually similar to experiments currently performed in undergraduate laboratories; however students collected different types of data using multi-sensory observations. The experiments themselves were developed by either: a) using chemicals that would provide different sensory changes such as the olfactory titrations, equilibrium and qualitative analysis experiments or b) capitalizing on sensory observations that were typically overlooked or ignored such as in the ASA kinetics, esterification and thermometric titrations. In order to develop these experiments, expected products and possible side reactions, which have different physical characteristics from the starting material were explored. These observations included distinct changes in aroma, color, precipitate formation (also be observed audibly with the light probe), temperature, and sounds ('popping' or 'fizzing').

ii) Hazards. Safety issues were taken into consideration, particularly since students rely on senses traditionally not employed in the laboratory setting. The hazards (MSDS data) and chemical properties were evaluated to determine exposure effects. The chemicals used were thoroughly screened and carefully compared for their effectiveness at various concentrations in order to determine their suitability for undergraduate labs. To be able to perceive the aroma of compounds, they must be volatile; however low inhalation toxicity is a requirement in teaching labs. In addition, aroma control and aroma fatigue were considered. Safety measures included wafting, chemicals placed in dropper bottles or in fume hoods to prevent environmental saturation, small scale experiments, and the use of smelling strips.

iii) Adoption measures. Materials and equipment were inexpensive and readily accessible to promote the adoption of these experiments. The experiments are comparable to traditional experiments in terms of preparation and teaching times as well as educational levels. To facilitate this, the set-up was generally simple. We used common household and commercial chemicals

usually found in undergraduate stock rooms, and the equipment was either currently utilized in traditional laboratories or inexpensively purchased. The hand-held fans were purchased for ~\$1 or less each. The Lumitest light probe was purchased for \$72 from the American Printing House for the Blind¹. A talking thermometer was purchased from the Royal National Institute of Blind People for \$20².

iv) Accuracy and precision of data. Rigorous testing was performed to validate that the results were as accurate and precise as traditional experiments. The experiments were also tested to establish experimental conditions necessary to fulfill the chemical objectives. The procedures were tested to ensure the observations would not give misleading results.

Pedagogical: The educational goals of this research project were fulfilled by implementing various educational approaches into the experimental design (Section 2.1) and included:

- i) Suitable educational framework used to develop the assessment, LLR.
- ii) Evaluation of misconceptions, terminology, and interventions to guide the development of the experimental procedure, conceptual questions and intervention measures.
- iii) Adoption of an investigative inquiry-based experimental approach with the promotion of collaborative work in performing the experiments.
- iv) Development of a laboratory format (LLR).

i) Educational framework. An educational framework was established, Marzano and Kendall's (M&K), to guide the development of educational goals and produce reasonable assessments specific to each experiment (Section 2.2). The framework chosen allowed for the incorporation of inquiry experimentation and was used as the foundation for the LLR. Critical thinking, self-analysis and knowledge construction were deemed essential to learning and were facilitated by the LLR.

ii) Evaluation of misconceptions and interventions. The literature on common misconceptions, issues with terminology and relevant interventions were investigated to develop the experimental procedure and pre- and post-lab conceptual questions. A variety of interventions were developed to remedy or prevent alternative conceptions. After the first implementation of the experiments, additional interventions were developed and some tested (ASA hydrolysis and thermometric titration experiments). Conceptual questions developed assessed students' understanding of the material and used methods such as analogies, word associations and pictorial representations.

iii) Investigation, inquiry and collaboration. Students demonstrated various cognitive skills as they investigated principles using multiple senses, made generalizations, analyzed data and utilized knowledge to draw conclusions. These processes are believed to encourage active-learners and promote critical thinking skills essential for scientists when evaluating a problem. These experiments were guided-inquiry (provided detailed experimental procedure but independently draw correct conclusions) or design-based inquiry (making choices on the experimental procedure). Students worked collaboratively in groups of 2-3 and as a class (esterification and titration pre-lab activity) in order to achieve a collaborative learning experience, however worked individually on their lab reports.

iv) Learning Lab Report. The LLR was developed, using the previous objectives, to promote reflective and critical thinking, enhance cognitive skills, and guide students writing construction (Section 2.3). The cognitive-centered format encouraged students to take more responsibility for their learning. The benefit to the instructor was the ability to monitor students' learning processes, provide guidance in difficult areas and modify the lab accordingly.

Multi-sensory learning can benefit *all* students by actively engaging them in learning through multi-sensory stimulation and reinforce learning as each sense builds toward a more

complete experience of a concept. This type of learning is often linked to more complex emotional responses of the brain (4,5) and Bauer has shown that students' attitudes towards chemistry are related primarily to their emotional response (6). From the results of the implementation of the experiments previously discussed in Chapter 3, students' expressed their interest in chemical determinations using different senses. Students' interest in the sensorial experiments or motivation towards learning the concepts may be engaged by the novelty of using multiple or different senses in making chemical determinations as our evidence suggests. According to the M&K theoretical framework (Chapter 2), self-system thinking (examination of importance, self-efficacy, emotions, and motivation) determines students' behaviors or actions in response to a new task or concept (7). A positive response to an intelligible and plausible new concept or task would lead to conceptual changes (8) and engage metacognitive thinking (setting and assessing of goals and monitoring clarity and accuracy of knowledge).

A study by Cacciatore and Seviau has shown that a single exposure to one inquiry experience led to enhanced performance relative to the content, and suggests that incremental additions can lead to greater improvements (9). This idea that exposure to a single experience can affect performance and the use incremental additions may provide even greater changes demonstrates evidence towards the benefits of using sensorial experiments with the LLR format. In sections 3.4 and 3.5, both single exposure to (SS students) and multiple experiences with (FS students) the LLR and sensorial experiments seemed to promote students' reflective thinking and thoughtful discussion of the concepts. Interesting studies that could evolve and extend from this work to support the rationale for these experiments and behavioral model of the theoretical framework (10) include:

i) *Sensorial vs. traditional laboratory formats*: The effects of how sensory learning incorporated in the laboratory improves the understanding of the experiment and increased

engagement may be evaluated through changes and differences in students' conceptual knowledge by assessing the impacts between controlled and experimental groups.

ii) *Uni- vs. multi-sensory* experiences: A correlation study between the use of a single sense vs. the combination of senses with respect to learning gains can be assessed to determine how each sense or a combination of them may affect students' effective learning.

The conceptual and reflective questions of the LLR evaluated students' thinking skills (10-12) and conceptions before and after reflection (13,14) on the experiment. For example, in the thermometric titrations (Section 3.5), students were able to re-evaluate their thoughts on acid strength and concentration as it related to a pictorial question (Figure 3.13). The majority of the students, who were unable to correctly answer this question before the reflective process, were able to correctly answer the question after the experiment with no assistance from the instructor. The results of the LLR indicated that this format promoted students' learning and critical thinking.

The data from this educational resource may be used to compare students' improvements in conceptual understanding of the material and their use of cognitive, metacognitive and self-system thinking skills (discussed in Section 2.2) (10). Other laboratory formats such as MORE and SWH formats could be used to compare any difference in learning gains between these formats (15), with the expectation that the LLR would provide more or at least the same improvements as the other validated formats. Studies of this nature can be compared with controlled groups and should include collection of background information, surveys related to reasoning ability, self-system and metacognitive thinking (16,17), examination of reliability and validity of the LLR questions to evaluate conceptual understanding (18).

Various controls were maintained during the implementation of the sensorial experiments described in Chapter 3 to preserve the quality and quantity of information given to the students prior to and during the experiments. These controls included:

1) The same general and organic chemistry professors taught the lecture portions of the courses, ensuring that the same material was covered during the lectures prior to the experiment, the experience and enthusiasm levels of the instructors were the same for each course.

2) The organic experiments (qualitative organic analysis and esterification) had the same laboratory instructor (researcher).

3) The same lab instructors were used for the various experiments or lab sections. The same two TAs served as the lab instructors for the FS general chemistry labs, after being trained by the researcher. The researcher was the instructor for the organic and SS general chemistry labs.

Based on the results of the implementation of the LLR, a couple of changes could be incorporated to increase the usefulness of the format. Reflective journaling could complement the LLR to observe conceptual changes over time as well as attitudes towards the sensorial experiments on a periodic basis. Reflective journaling in the classroom has been used as an effective tool in critical thinking, interpersonal skills, and problem solving skills (14). Reflective videos have been used to improved students' process skills in the laboratory, but not used to improve conceptual knowledge (19). To aid students' ability to provide reasonable conceptual driven responses, a problem solving technique such as the GOAL (gather, organize, analyze and learn) protocol may be used as well (20).

These sensorial experiments not only provided an opportunity for students to explore chemistry through engagement of different senses, but could also give an opportunity for sensorially disabled students to participate in chemistry laboratories. These experiments could fill gaps in the chemistry curriculum that do not allow for disabled students, particularly those with visual difficulties, to work independently, if at all in a chemistry lab environment. Including these sensorial experiments into the chemistry curriculum could allow students with impairments to participate in the laboratory alongside their non-disabled classmates, which might change misguided opinions and

demonstrate the ability inherent in everyone to contribute to and enjoy science. The potential application of the sensorial experiments with disabled students, adaptations and evaluation of learning gains from the LLR and sensorial experiments are discussed in Section 4.2.

4.2 Sensory adaptations

The sensorial experiments have shown the utility of the senses in the undergraduate laboratory (Section 1.3). However, during the implementation of these experiments, a few students exhibited sensory problems. These included the difficulty with color changes such as clear to pink with the Phenolphthalein indicator (equilibrium and titration demonstrations) and the inability of 28% and 25% of male students to perceive methanol and ethanamide respectively (qualitative organic analysis, Section 3.2). These problems did not hinder the students' active participation, as they were able to use multiple or different senses in these experiments, allowing students to still be able to make determinations and contribute to the laboratory. Taking advantage of multi-sensory learning could allow sensory disabled students to perform and benefit from the sensorial experiments. The use of sensorial experiments with students with disabilities to make chemical determinations has not been explicitly explored. The development of additional sensorial experiments to follow the progression of the general chemistry and organic courses would provide laboratory experience throughout the entire laboratory course. To utilize these experiments, various adaptations may be needed to provide a fair environment for these students. An insight into how persons with sensory disabilities utilize their other senses, what they may perceive using these senses and how it may apply to the sensorial experiments is of interest.

It is often said that when someone has a sensory disability, the others senses become more heightened or the acuity increases due to cortical reorganization (21) and some research suggests that a disability in one sense leads to improvement in others due to expanded sensory areas of the brain

(22). However, it has not been proven that the other senses function better in people with disabilities, but rather they are able to focus more energy on the remaining senses to assist their daily tasks (23) and get a somewhat complete perception of their experiences. These ideas are often taken advantage of to aid persons with sensorial disabilities. Persons who have visual impairments often utilize other senses to aid them such as using fingers to read Braille or paying attention to sounds and vibrations to know when to cross the street.

Fingertips are useful for observations in people with visual disabilities and their acuity and precision can often be unrecognized by persons without visual disabilities (24). The sensitivity of the sense of touch, discussed in Section 1.3, allows for perception of small changes in temperature, pressure, vibrations, and the ability to use active touch to determine texture, hardness, shape, volume, and weight. These haptic observations allowed chemistry students to make conclusions about the reactions in the sensorial experiments such as to determine the degree (qualitative judgment) and direction (exothermic and endothermic) of enthalpy changes. Visually-disabled persons, in particular, have been able to discern with great detail shapes, texture, and spacing of objects (spatial discrimination) (24). Braille is a system of raised dots that utilized these facts to allow visually disabled to read text and experienced Braille readers can read ~100 words/minute, which is slower than visual readers, but considered impressive (22). Dr. Geerat J. Vermeij, a biologist, utilizes vibrations made by fingernails to determine the topography of shells such as spacing and structure (24). The sense of touch was utilized in the experiments to qualitatively determine changes in temperature as an indicator of enthalpy changes.

Other blind researchers have been able to use various techniques to aid them in performing their research or have provided new avenues for blind students to pursue science such as a haptic device that conveys location on scientific plots or weather maps, speech programs (such as JAWS and Audio System for Technical Readings) to hear text and mathematical notations, and laser

stereolithography for constructing 3D replicas of molecules from computer graphics (25). Sound is useful to locate objects and judge distances by use of echoes, changes in vocalization, and footsteps. The wide range of frequencies that can be detected by the ear and sensory perception of these sounds gives us the ability to make judgments on distance of sounds, identification of direction and changes in volume and tone (Section 1.3). This makes the sense of hearing useful in making determinations with sound changes in the laboratory such as hearing light probe intensity changes or the fizzing due to the evolution of gases.

Persons who are deaf can reportedly locate moving objects faster than hearing persons due to enhanced visual performance when responding to visual stimuli, however there is research indicating that there is no difference in the visual sensitivity between hearing and deaf persons (4). This increased ability is thought to be a result of and primarily related to the visual method of communication used by deaf persons. Persons who are deaf typically use sign language to manually communicate and the signs depend on the shape, orientation and movement of hands and arms in conjunction with facial expressions. Vision is one of the most utilized of the senses in chemistry laboratories and was used in the sensorial experiments to determine color, shade and clarity changes.

People have a tendency to underestimate the importance of olfaction, which makes it more difficult for persons with various types of anosmia (partial to complete) to receive the same types of aid as someone who has lost other senses. Persons with olfactory disabilities may experience depression due to the sentimentality of aromas and the quality of their life may be also affected (26). This problem not only affects the protective and recognition properties of olfaction, but also the ability to enjoy typical aromas and flavors of food. As seen in Section 3.2, 20% of the students experienced the inability to observe one or two aromas in the qualitative organic analysis experiment. The use of a variety of aromas in the first portion of the experiment allowed students to still make a considerable number of olfactory observations. The multi-sensory portion of the

experiment allowed these students to actively observe chemical changes from the confirmatory tests without difficulty. With the low incidence of varying types of anosmia (1-2% of the US population), the sense of smell is a strong candidate in making chemical determinations of aroma changes and identification of compounds. We can perceive many aromas at low concentrations, associate the aromas of chemicals with every-day items and distinguish enantiomers (such as *R* and *S*-carvone). The sensitivity of the nose and the varying odor thresholds of chemicals (Section 1.3) make the sense of smell accurate enough to make these determinations in an undergraduate laboratory.

Attention has otherwise been placed on customized instrumentation or laboratory accommodations to aid the lab deficiencies for students with disabilities. Neely describes a project, undertaken by the University of Colorado, to investigate the use of assistive technology devices and equipment modifications that could promote students with disabilities to work independently (27). The equipment that was evaluated included displaying a magnified image captured by a camera, using plastic rather than glass equipment and instruments with audio alarms. These were examined for their usefulness to students with disabilities as well as for their cost. Supalo et al. have also presented adaptations which include a notched plastic syringe, submersible audible light sensor, and low cost materials that can be used to provide tactile observations for laboratory and lecture courses. These items promote inclusion by providing accessibility for students who are blind or have low vision (28). In addition, the importance of laboratory assistants to aid visually disabled students is commonly discussed as well as the arrangement of the laboratory in order to maximize the productivity of the students (29-31).

The American Chemical Society Committee on Chemists with Disabilities have published a manual for teaching chemistry to student with various disabilities, outlining modifications and requirements of the instructor and student to provide a productive laboratory and lecture environment (32). The manual includes architectural modifications for wheel chairs and laboratory equipment

modifications for visually and hearing impaired students. The requirements of the instructor and students include good and advance communications, so that the modifications and accommodations can be taken care of. However, students with visual disabilities who are not allowed to actively participate in the laboratory or depend on assistants may be discouraged from considering science careers (33). Smith suggests allowing students to explore the chemistry laboratory with the aid of a reader, but suggests they should not be hindered from exploring but rather they should utilize their other senses to make observations (34).

Students with disabilities may use alternative methods to perceive the world around them which may create deficits or enhancements to their understanding of chemical concepts. Jones et al. have shown that students with visual impairment were more accurate with measurements on large and small scales (human measurements) (35). They suggest that these students either have more experience with these sizes or utilize information about size more causing them to remember it longer than their normally sighted students. However, visually impaired students had greater difficulty with very large and very small scales as they use their other senses to develop conceptions of size and distance. The effectiveness and learning gains of our sensorial experiments for students with sensorial challenges should be evaluated to determine how their experience using different senses in their daily lives may affect their conceptualization of the experiment.

In order to utilize the sensorial experiments with students with disabilities, adaptations such as the use of modified chemical glassware and instrumentation is needed in order to facilitate learning of chemistry techniques. The literature previously discussed demonstrates a range of suggestions for and implementation of adaptive technologies and equipment for students with disabilities. Some of these requirements are already incorporated in our sensorial experiments. The use of dropper bottles would benefit students with neuromuscular disabilities and are ideal for students with vision disabilities for its easiness in dispensing liquids. The utilization of fans

(esterification and ASA kinetics) to circulate aromas in our experimental set-up allows blind students to correctly position themselves when conducting experimentation. The use of small amounts of chemicals reduces exposure to harmful chemicals and prevents potential accidents. However, scaling up the experimentation may also be beneficial for students who are unable to manipulate small glassware (neuromuscular disabilities) or make sensory observations with small quantities of chemicals or small scale reactions.

Various general adaptations exist to make audible observations such as the light probe and talking instruments which can be purchased inexpensively (discussed in Section 4.1). An example of these adaptations that we tested is the Lumitest light probe¹ which emits a tone that is relative to the amount of light detected and can convert light into approximately 1000 different acoustic signals which can be observed using the device. This instrument transforms brightness into high frequencies, low light into low signals and the absence of light produces no sound. The user can locate a light source in a room, determine whether an LED is flashing or determine changes in clarity or significant differences in color. The ETI talking thermometer², purchased for the sensorial experiments, reports the measured temperature audibly and had a temperature range of -19.9 to +119.9°C (Figure 3.27). To hear the temperature, the talk button is pressed and the thermometer instantly tells the current temperature.



Figure 3.27. ETI talking thermometer.

In conclusion, six sensorial experiments have been developed, of which five have been implemented into our teaching laboratories. The sensorial experiments implemented worked effectively to provide accurate data from which students were able to draw correct conclusions. The LLR, lab report format, was developed to align with the pedagogical goals and utilized with three of the experiments. These sensorial experiments not only are mentally stimulating by increasing attention to the concepts, but the use of the LLR in conjunction with the experiment promotes reflective thinking and enhance cognitive skills. These experiments may also fill gaps in the chemistry curriculum that do not allow for visually disabled students to work independently, if at all by providing an opportunity for visually disabled students to participate in various chemistry laboratories.

Notes:

¹Lumitest Probe: Catalog #: 1-03956-00; <http://sun1.aph.org/starweb/APHBLLouis/servlet.starweb>, (accessed July 2008).; Light probe and Colour Sensors, updated February 21st, 2008, http://www.tiresias.org/research/devices/light_probes.htm; Network of Care for Developmental Disabilities – Hannibal Regional Office, 2008, <http://hannibal.mo.networkofcare.org/dd/assistive/abledata.cfm?pageid=19327&top=13326&productid=158676&trail=22,13134&discontinued=0>; (accessed September 2008).

² Talking Food thermometer, Product #DK115, http://onlineshop.mib.org.uk/display_item.asp?n=11&c=45&sc=128&id=2839&it=1&l=3&d=0; (accessed January 2009).

REFERENCES

1. Wood, J. T.; Eddy, R. *J. Chem. Edu.* **1996**, *73*, 257–258.; Neppel, K.; Oliver-Hoyo, M. T.; Queen, C.; Reed, N. *J. Chem. Edu.* **2005**, *82*, 607.; Flair, M.; Setzer, W. N. *J. Chem. Edu.* **1990**, *67*, 795–796.; Rancke-Madsen, E., Krogh, J.A. *Acta Chem. Scand.*, **1956**, *10*, 495-499.
2. Ratliff, J. L. *J. Chem. Edu.* **1997**, *74*, 710.
3. Jones, G. M.; Andre, T.; Superfine, R.; Taylor, R. *J. Res. Sci. Teach.*, **2003**, *40*, 303.
4. Santangelo, V., Spence, C. *J. Exp. Psychology: Human Percep. Perform.*, **2007**, *33*, 1311–1321.; Moats, L. C., Farrell, M. L., Multisensory Instruction In *Multisensory teaching of basic language skills*, Birsh, J. R. Paul H. Brookes Publishing Co., MA, 2000. Chapter 1.; Bresciani, J., Dammeier, F., Ernst, M. O. *Brain Research Bulletin*, **2008**, *75*, 753–760.; Cann, A., Ross, D. *Amer. J. Psychol.*, **1989**, *102*, 91-102.; Chu, S.; Downes J. *Mem. Cognit.*, **2002**, *30*, 4, 511–518.; Buchanan, T. W. Tranel, D., Adolphs, R. *Learn. Mem.* **2003** *10*: 319-325.; LeDoux, J. E. *Current Opinion in Neurobiology*, **1992**, *2*, 191-197.
5. Lowery Bretz, S. *All Students are Not Created Equal: Learning Styles in the Chemistry Classroom*, Eds. Pienta, N. J., Cooper, M. M., Greenbowe, T. J. Chapter 3, in *Chemists' guide to effective teaching*, Pearson Education Inc., NJ, 2005.
6. Bauer, Christopher F. *J. Chem. Edu.* **2008**, *85*, 1440.
7. Bandura, A. *Psychological Review*, **1997**, *84*, 191-215.; Malmivuori, M. *Educational Studies in Mathematics*, **2006**, *63*, 149-164.
8. Posner, G. J.; Strike, K. A.; Hewson, P. W.; Gertzog, W. A. *Science Education*, **1982**, *66*, 211–227.
9. Cacciatore, K. L.; Sevia, H. *J. Chem. Edu.* **2009**, *86*, 498-505.
10. Marzano, R.J., Kendall, J.S. *The New Taxonomy of Educational Objectives*, 2nd Ed. 2007, Corwin Press, California.; Marzano, R.J., Kendall, J.S. *Designing & Assessing of Educational Objectives: Applying the New Taxonomy*, 2008, Corwin Press, California.
11. Cracolice, M. S. *How Students Learn: Knowledge Constructions in College Chemistry*, Eds. Pienta, N. J., Cooper, M. M., Greenbowe, T. J. Chapter 2, in *Chemists' guide to effective teaching*, Pearson Education Inc., NJ, 2005.
12. Tan, K. S., Goh, N. K., Assessing Students' Reflective Responses to Chemistry-Related learning Tasks, Paper presented at IAEA 2008 Annual Conference, Cambridge UK.
13. Lerch, C.; Bilics, A.; Colley, B., Using Reflection to Develop Higher Order Processes, Paper presented at the Annual Meeting of the American Education Research Association, San Francisco, CA, 2006.

14. Mabrouk, P. A. *Active Learning: Models for the Analytical Sciences*, Oxford University Press, 2007.
15. Rudd, J. A., II; Greenbowe, T. J.; Hand, Brian M. *J. Chem. Edu.* **2007**, *84*, 2007.; Poock, J. R.; Burke, K. A.; Greenbowe, T. J.; Hand, B. M. *J. Chem. Edu.* **2007**, *84*, 1371.; Tien, L. T.; Teichert, M. A.; Rickey, D.. *J. Chem. Edu.* **2007**, *84*, 175.
16. Classroom Test of Scientific Reasoning;
<http://www.public.asu.edu/~anton1/AssessArticles/Assessments/Science%20Assessments/Scientific%20Reasoning%20Test.pdf>; (accessed Mar 2009).; Cracolice, M. S.; Deming, J. C.; Ehlert, B. *J. Chem. Educ.* **2008**, *85*, 873.
17. Bauer, C. F. *J. Chem. Edu.* **2005**, *82*, 1864-1870.; Oliver-Hoyo, M. T.; Allen, D.. *J. Chem. Edu.* **2005**, *82*, 944-949.; Eddy, R. M. *J. Chem. Edu.* **2000**, *77*, 514-517.; Shibley, Ivan A., Jr.; Zimmaro, Dawn M. *J. Chem. Edu.* **2002**, *79*, 745-748.; Cooper, Melanie M.; Sandi-Urena, Santiago. *J. Chem. Edu.* **2009**, *86*, 240-245.
18. Bord, W. R., Gall, M. D. *Educational Research, An Introduction*, 5th Ed., Longman Inc., 1989.
19. Veal, W. R.; Taylor, D.; Rogers, A. L. *J. Chem. Edu.* **2009**, *86*, 393-398.
20. GOAL Problem Solving, http://www4.ncsu.edu/~beichner/info/tips/Problem-Solving_Strategy.html; (accessed April 2009).; Oliver-Hoyo, M. T.; Justice, J. *J. Coll. Sci. Teach.*, **2008**, *37*, 62-67.
21. Finney, E. M.; Dobkins, K. R. *Brain research. Cognitive brain research*, **2001**, *11*, 171-183.
22. Goldstein, E.B. *Sensation & Perception*, 5th ed. Brooks/Cole Publishing Company, California, 1999.
23. Goldreich, D., Kanics I. M. *J. Neuroscience*, **2003**, *23*, 3439 –3445.
24. Vermeij, G. J. *J. Hand Surgery*, **1999**, *24*, 215-8.; To Sea with a Blind Scientist, <http://nfb.org/legacy/books/kernel1/kern0610.htm>, (accessed April 2009).
25. Wang, L. Seeing the Possibilities, *C&EN News*, **2007**, *85*, 36-40.; Opening New Vistas for Blind Scientists, *Science*, **1998**, *282*, 37.; Blind chemists provides tools for peers, http://www.collegian.psu.edu/archive/2007/10/23/blind_chemist_provides_tools_f.aspx.; Chemistry by Touch, *Science News*, **1995**, *145*, 122-123, <http://www.sciencenews.org/pages/pdfs/data/1995/147-08/14708-12.pdf>, (accessed April 2009).
26. Temmel, A. F. P.; Quint, C.; Schickinger-Fischer, B.; Klimek, L.; Stoller, E.; Hummel, T. *Archives of otolaryngology: head & neck surgery*, **2002**, *128*, 635-41.
27. Neely, M. B. *J. Chem. Edu.* **2007**, *84*, 1697-1701.

28. Supalo, C. A.; Mallouk, T. E.; Rankel, L.; Amorosi, C.; Graybill, C. M. *J. Chem. Edu.* **2008**, *85*, 243-247.
29. Supalo, C. *J. Chem. Edu.* **2005**, *82*, 1513-1518.
30. Pence, L.E.; Workman, H. J.; Riecke, P. *J. Chem. Edu.* **2003**, *80*, 295-298.
31. Crosby, G. A. *J. Chem. Edu.* **1981**, *58*, 206.
32. Miner, D. L.; Nieman, R.; Swanson, A. B.; Woods, M.; Carpenter, K. (Editors), *Teaching Chemistry to Students with Disabilities: A Manual for High Schools, Colleges, and Graduate Programs*, American Chemical Society Committee on Chemists with Disabilities. 2001. <http://membership.acs.org/C/CWD/TeachChem4.pdf>, (accessed November, 2007).
33. Wang, L. *C&EN*. **2007**, *85*, 30, 36.
34. Smith, D. *J. Chem. Edu.* **1981**, *58*, 226-227.
35. Jones, M. G.; Taylor, A. R.; Broadwell, B. *J. Res. Sci. Teach.*, **2009**, 1-14, Early view - published online. <http://www3.interscience.wiley.com/cgi-bin/fulltext/121622598/PDFSTART>; (accessed March 2009).

APPENDICES

Appendix A . Publications.....	Error! Bookmark not defined.
Appendix B . Qualitative Organic Analysis Experiment.....	Error! Bookmark not defined.
Appendix C . Esterification Kinetics Experiment	Error! Bookmark not defined.
Appendix D . Le Chatelier's and equilibrium study	Error! Bookmark not defined.
Appendix E . Acetyl salicylic Acid Kinetics Experiment.....	Error! Bookmark not defined.
Appendix F . Thermometric Titrations	Error! Bookmark not defined.
Appendix G . Olfactory Acid-Base Titrations.....	
.....	Error! Bookmark not defined.

Appendix A. Publications

A Qualitative Organic Analysis That Exploits the Senses of Smell, Touch, and Sound

Bromfield-Lee, Deborah C.; Oliver-Hoyo, Maria T.
J. Chem. Edu. **2007**, *84*, 1976.

A Qualitative Organic Analysis That Exploits the Senses of Smell, Touch, and Sound

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Qualitative organic analysis is the identification of organic functional group(s) in a compound. Since some functional groups impart characteristic aromas, this experiment explores how the sense of smell can be used as a discriminating tool in identifying the functional group in an unknown. In addition to describing odors and characterizing functional groups by certain smells, students perform confirmatory tests that rely primarily on the senses of touch and sound. Typical procedures were modified to employ multiple senses taking advantage of all the physical changes that take place in the reaction between the functional group and the test reagent. The use of a light probe (LP) enables students to qualitatively analyze many visual changes as an auditory response. Students "hear" significant changes in color, solution viscosity, and the presence of a precipitate.¹

Experimental Overview

A variety of compounds were chosen for their distinct odors and were tested to decide the suitability in using them in a teaching laboratory environment. For each functional group one or two safe and easy confirmatory tests were chosen after extensive testing. As written, this experiment was tested by four organic laboratory sections (65 students) and all procedures and instructor's notes can be found in the Supplemental Material.^W

In preparation for the lab, students make a chart of various functional groups giving an example molecule of each. In the lab, students use their sense of smell to characterize the aromas by testing known functional groups and formulate descriptive categories of smells for each functional group. Students work in groups of 2 or 3 to compensate for any student who is unable to smell certain chemicals. Students then use their own olfactory classification scheme to determine which functional group their unknown compound has and which confirmatory tests are needed to confirm their assertion (Scheme 1). The

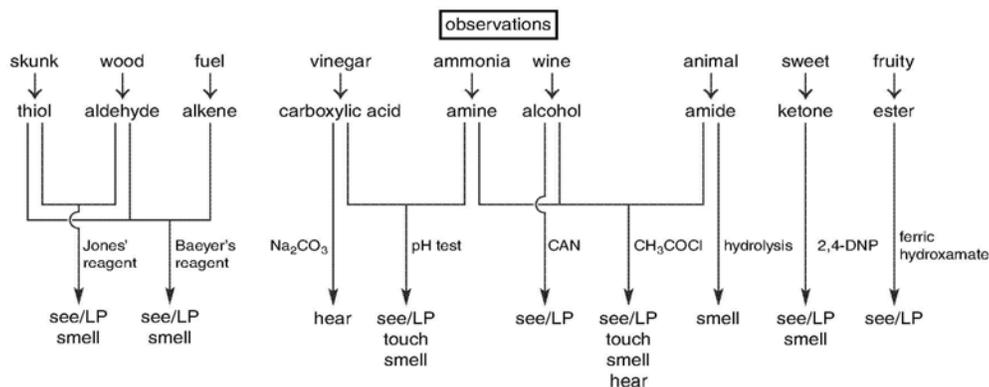
chosen confirmatory tests produce distinct changes (1), which are monitored by one or more senses. This approach encourages students to discuss aromas they may have trouble identifying, to use adjectives that truly characterize their groups, and to examine their olfactory findings to decide on confirmatory testing. Confirmatory tests for the different functional groups utilize the senses of touch (generation of heat) or sound (produced in the chemical reaction or via the use of a light probe) promoting the use of senses usually neglected in laboratory procedures.

Each group may be given their own set of known chemicals or several workstations may be set up. The more odorous compounds are placed in the hood along with the test reagents. The instructor must show and monitor how to properly smell by wafting and how to use a light probe (Lumitest light probe purchased from the American Printing House for the Blind Inc.) to identify changes in color, viscosity, and formation of a precipitate.

Students are expected to write a brief procedure, results, conclusion, and answer post-lab questions. The experiment can be completed in an average of two hours. Characterization by spectroscopic methods such as IR and NMR may be used to supplement this sensorial qualitative analysis. More advanced students may discuss the mechanisms involved in these reactions (see the Supplemental Material^W).

Practical Considerations

To avoid contamination, the testing reagents and sample compounds are placed in small glass dropper bottles. Strips of filter paper, similar to smelling strips, are used to allow students to waft the compounds (preventing students from directly inhaling from the bottle). The toxicity of all compounds was evaluated for the effects of inhalation. The known and unknown samples used in this experiment do not exhibit effects on the lungs at



Scheme 1. Example procedure for olfactory classification and sensorial chemical test confirmation. LP is light probe.

moderate levels. Some of the compounds show only minor effects with contact to skin. It is still advisable to have the students close all bottles tightly after use.

Coffee crystals are made available for the students to smell between compound identification. This is a recommended procedure to "clean" the sense of smell. Some students took advantage of this while others did not think it was necessary. However, those that used the coffee crystals to cleanse their nasal passage during the experiment stated it helped to differentiate better the various aromas.

Studies have shown that people recall with greater accuracy odors over longer periods of time than things that they see (2). This fact is exploited as students are asked to be creative in describing the compounds and to remember the functional groups by descriptive aromas. As the senses of smell, sound, and touch take priority in this experiment, it is suitable for visually impaired students to perform it in an active and meaningful manner. The use of dropper bottles is also ideal for students with vision disabilities for its ease in dispensing liquids. Visually able students are also stimulated as they engaged in ways not usually employed in laboratory settings. The students are not only using multiple senses to perform the lab, but also devising their own experimentation. The experiment is designed to be an inquiry-based lab, in which the students decide on which confirmatory tests are needed based on their classification of aromas and the relationship to functional groups.

General Hazards

All corrosive reagents used, such as oxidants [CrO_3 , K_2MnO_4 , $\text{Fe}(\text{NO}_3)_3$, and CAN^2], strong acids and bases (HCl

and NaOH) and acetyl chloride, should be handled with proper care to avoid severe burns. Chromium is carcinogenic. Potentially flammable reagents include the alcohols, ketones, aldehydes, thiols, amines, and alkenes. These should be at safe distances from ignition sources. Owing to the strong aromas some reagents may have (such as aldehydes and thiols), wafting is the only acceptable technique used throughout this experiment. Amines are incompatible with oxidizing agents, may cause burns, and may have strong odors that may cause burning sensation if inhaled directly. Extreme prolonged exposure to thiols may be toxic to the liver and kidneys. Ethanamide is hydroscopic and excessive prolonged exposure may cause damage to the liver. Suggested reagent concentrations, the use of filter paper as smelling strips, and wafting technique permit the safe use of the sense of smell in this experiment. Follow tested procedures (stated in the Supplemental Material^(U)) as extreme prolonged exposure to some compounds can be irritating or hazardous.

Results

Students were able to detect and characterize the known compounds; however, some required a bit of assistance in grouping together the compounds with the same functional groups. Correlations between the functional group and characteristic aromas allowed students to identify the functional groups of their unknowns. Students came up with a wide range of descriptions and used very interesting adjectives in their characterization. Examples of students' descriptions are shown in Table 1.

Students showed differences in opinion about an odor in terms of what smelled good or bad, but were able to identify the variety of functional groups. Only 3 out of 65 students

Table 1. Odor Characterization by Students

Compound	Sample of Students' Characterizations
Methanol	Bananas, sweet alcohol, wet paint, fresh dirt, wet feet, citrus, weak Pine-Sol.
Ethanamide	Feet, body odor, eggs, old person's house, wet dog with vinegar, old book.
Formaldehyde	Almond, sesame oil, Fritos chips, latex paint, Target, after effect nostril burning.
Cyclohexanone	Soap in public bathrooms, doctor's office, paint thinner, cherry cough drops.
Acetic acid	Vinegar, glue, rotten feet, nursing home, urinal tablet, cement.
Butylamine	Bleachy chlorine, ammonia, horse urine, hair perm, rotten fish, tuna.
Butanethiol	Bad garlic, rotten or burned pumpkin seeds, sweetener.
Hexene	Cheap fruity perfume, gasoline, nail salon, paint thinner, rotten vegetables.
<i>n</i> -Propyl acetate	Permanent marker, glue, nail polish remover, onion, mineral spirits.
Ethanol	Disposable lab gloves, hair product (dye), gin, vodka, Pine-Sol or Clorox.
<i>N</i> -methylacetamide	Dirty diaper, stinky boy's locker room, nursing home, rotten flower.
Butyraldehyde	Vomit, fried plantains, burning Play-Doh, rotten wood, fake cheese.
Acetone	Moldy moth-balls, acetone, permanent marker, cheap vodka, rubber cement.
Citric acid	Weak acid, burning tires, stale, musty old attic, faint cheese, faint sour.
Diethyl amine	Dead animal, urine, awful ammonia, bleach, rotten fish, old antifreeze.
1-Octanethiol	Burned rubber in a field of flowers, onion/garlic/chive/skunk combo, bad chips.
Cyclohexene	Gasoline station, car exhaust, vinyl, burning Legos, department store, death.
Ethyl acetate	Acetone, reminding of salicylic acid, permanent marker, vinegar.

had difficulty characterizing any of their compounds owing to allergies or a pre-disposed condition. More male students than females had difficulty in detecting certain smells. Methanol, *N*-methylacetamide, citric acid, and ethanamide were difficult for some of the students to identify. Eleven out of 40 males (28%) reported that methanol had no smell, while no females appeared to be unable to discern this odor. Two out of 25 females (8%) could not detect any aroma from ethanamide, while 10 out of 40 males (25%) did not detect the ethanamide. In general, males had difficulty distinguishing and characterizing particularly sweet or pleasant odors (3–5).

Some student comments were enlightening as to their experience in the lab. Examples include

- This lab really surprised me on how accurate using your senses could actually be. I think this was a great lab (even though some of the material offended the senses)...
- I liked this lab the most out of all the labs we have had this semester. It was an easy-to-follow procedure and I have a lot of fun trying to figure out the functional groups. Some of the smells were a bit strong, but it was still very interesting and I learned a lot.
- I felt this was a very fun lab. Very interesting and felt that I could relate it to my everyday life. I felt this was the best lab of the semester.
- I thought this was an informative lab experiment to show how important our sense of smell can help in everyday chemistry.

Conclusion

Owing to the differences shown by males and females it is recommended that each group be composed of at least one male and one female. It is vital that the students waft the compounds properly so that they do not become saturated with the aromas. Using the filter paper as smelling strips is a good way to decrease the strength of many of the compounds. Students who used the light probe were able to connect an auditory representation to the visual changes observed.

Based on the performance of the students in the laboratory as well as on their write-ups, it can be concluded that this sensorial lab can add richness to traditional organic laboratories. Students were able to group compounds by their functional group characteristic smells, utilize their own classification to decide on necessary confirmatory tests, and utilize effectively the senses of touch, sound, and smell to identify their unknowns.

In addition, students' feedback strongly stated they enjoyed the experiment especially discovering for themselves the functional group involved.

Acknowledgments

The authors would like to thank Maria Gallardo-Williams for incorporating this experiment into the laboratory schedule and her organic students who enthusiastically tested these procedures. This work has been made possible by the generous support of the National Science Foundation via CAREER Award No. REC-0346906.

Supplemental Material

Experimental protocols for the students, detailed notes and hazards for the instructors, and proposed mechanisms for each reaction used are available in this issue of *JCE Online*.

Notes

1. For students unable to view changes in color or intensity, a light probe may be used. The light probe can distinguish these changes by detecting changes in light passing through the test tube and emitting different frequencies or sound.
2. CAN is ceric ammonium nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.

Literature Cited

1. (a) Shriner, Ralph L.; Herman, Christine F.; Morrill, Terence C.; Curtin, David Y.; Fuson, Reynold C. *The Systematic Identification of Organic Compounds*, 8th ed.; John Wiley and Sons, Inc.: Hoboken, NJ, 2004. (b) Griswold, John R.; Rauner, Richard A. *J. Chem. Educ.* 1991, 68, 418–420. (c) Solomons, T. W. Graham; Fryhle, Craig B. *Organic Chemistry*, 7th ed.; John Wiley and Sons, Inc.: New York, 2000. (d) Bruckner, Reinhard. *Advanced Organic Chemistry: Reaction Mechanisms*; Harcourt Academic Press: San Diego, 2002. (e) Silvert, D. J. *J. Chem. Educ.* 1987, 64, 971–972.
2. Savic, Ivanka. *Curr. Opin. Neurobiol.* 2002, 12, 455–461.
3. Doty, Richard L.; Kerr, Kara-Lynne. *Neuropsychologia* 2005, 43, 1749–1753.
4. Doty, Richard L.; Applebaum, Steven; Zusho, Hiroyuki; Settle, R. Gregg. *Neuropsychologia* 1985, 23, 667–672.
5. Doty, Richard L. Psychophysical Measurement of Odor Perception. In *The Human Sense of Smell*; Laing, D. G., Doty, R. L., Breipohl, W., Eds.; Springer-Verlag: Berlin, 1992; pp 91–134.

An Esterification Kinetics Experiment That Relies on the Sense of Smell

Bromfield-Lee, Deborah C.; Oliver-Hoyo, Maria T.
J. Chem. Edu. **2009**, *86*, 82.

An Esterification Kinetics Experiment That Relies on the Sense of Smell

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The sense of smell, along with the senses of touch and hearing, are under-utilized tools in chemistry laboratories. Even though chemistry explores everything we perceive through our senses, eyesight alone has been the primary means for analysis and investigation of chemical concepts in most teaching laboratories. Students outside the classroom, however, explore their world with all their senses, hence performing chemical experiments with multiple senses in a safe way should be a natural process.

There are few experiments that utilize multiple senses to perform chemical experimentation in teaching laboratories. Some examples include olfactory titrations that use the sense of smell to determine endpoints (1–3), haptic technology that uses the sense of touch to explore the microscopic world (4), and experiments that use sound to determine the conductivity of various materials (5). These types of experiments are particularly useful to students with visual impairments. More efforts have been placed on modifications in glassware, use of sighted assistants, and planning for safety and convenience in accommodating students with disabilities in the laboratory (6). Attention has also been paid on customized instrumentation as in the case of conductivity titrations where the endpoint is detected audibly (7, 8), and the use of the photosensitive Optacon that translates images into vibrations (9). Manipulation of typical chemical experiments to involve multiple senses can be mentally stimulating for students owing to the potential for better memory retention (10, 11). These types of experiments become particularly useful for students who are visually disabled as these references suggest.

The experiment described in this article involves a Fischer esterification synthesis by which students explore the time taken for a critical concentration of the ester to form and then be observed by smell. Various factors are investigated including the concentration of the carboxylic acid and the amounts of the catalyst or alcohols added. The kinetics in relation to the

molecular structure is studied by changing the types of alcohols (12, 13) or carboxylic acids (14) or both and comparing various chain lengths and branching. Traditionally, these types of studies are performed spectroscopically (15–17). Since many esters have naturally occurring aromas that are pleasant and easily recognized (18), this experiment studies esterification kinetics using the sense of smell to detect the emergence of the ester aroma formed during the reaction.

Experimental Procedure

The experimental procedure is organized into three parts. During Part A of the experiment, students synthesize a variety of esters individually and categorize them by aromas (Scheme I). Each student is assigned an ester to synthesize and must collect all other classifications from the lab participants.

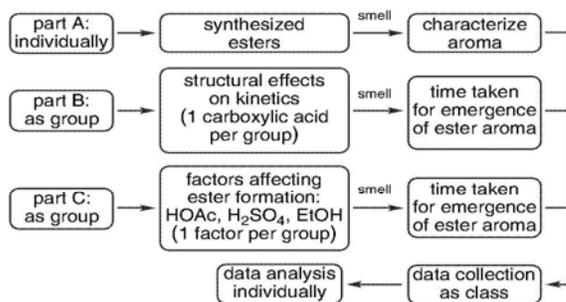
In Part B, groups consisting of 2–3 students are assigned a carboxylic acid with which they react with 4 alcohols. Students monitor the time it takes for emergence of the ester aroma for their assigned carboxylic acid with each alcohol recording the data in seconds. The students collect the data of the other carboxylic acids from all groups to complete a table and analyze the effect of each reagent.

Part C of the experiment involves monitoring the emergence of the ethyl acetate aroma while varying the ethanoic acid concentration, amount of the alcohol, or the amount of the catalyst (concentrated sulfuric acid). Each group is assigned one factor to vary and the remainder of the data is collected from the other groups. The students gather data to draw conclusions on the structure–activity relationships and factors affecting the reaction via leading questions asked at the end of the experiment using Parts B and C.

Students are expected to write a brief procedure, report their results, and answer post-lab questions in an average of two hours and thirty minutes. The experiment is written as an inquiry-based laboratory where students explore the topic with minimal instruction and are asked to draw conclusions on the nature of the esterification reaction. Four first-semester organic laboratory sections (89 students) tested this experiment and the procedures; instructor notes and results can be found in the online material. The students use typical laboratory equipment and reagents with the exception of a hand-held battery powered fan, which can be purchased inexpensively.

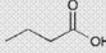
Experimental Considerations

A wide variety of chemicals used in this experiment had been screened for effectiveness in the reaction as well as for safety. The volatility and odor detection thresholds for the esters produced in this experiment were compared and found to have similar vapor pressures and detection concentrations. A table comparing odor thresholds and molar masses of potential esters can be found in the online material.



Scheme I. Flow chart of the experimental procedure.

Table 1. Student Descriptions of Aromas for Part A

Acids	Alcohols					
						
	Rubber	Flowers, apricot	Peaches, glue, new shoes, soap	Fruity glue, lemon, marker, runts candy	Fruit, lemon, crisp linen, moonshine, sweet, melon	Ether-like, rubber, flowers, fabric softener
	Alcohol, marker, paint thinner	Cucumber, grapes, rubber cement	Pears, hair spray, fruit	Rum, pears, glue	Elmer's glue, liqueur, apple	Fruit smell, marker, citrus
	Banana alcohol, pineapple	Sour apple	Cheese, markers	Old fruit, marker, apple	Cherry, strawberry, apple, banana, grapes	Paint, bubble gum
	Citrus, feet, rubbing alcohol	Apple, feet	Apples, rum, hair spray	Banana, banana chips, strawberry, pineapple	Apples, pineapple, grape	Pears, bubble gum, strawberry

Inhalation

The toxicity of all compounds was evaluated for the effects of inhalation using their available MSDS. The reagents used in this experiment do not exhibit effects on the lungs at moderate levels. However, the procedure for wafting should be demonstrated and used since direct inhalation of any chemical may cause irritations. Coffee crystals are made available for the students to smell between trials as a suggested procedure to "clean" the sense of smell. Promptly discarding waste chemicals between trials is beneficial in keeping the laboratory free of aromas.

Fans were used to circulate the ester aroma, which allows students to smell the aromas from a safe distance. Students position the apparatus at a particular distance in which the aromas are strong enough to detect, but not overwhelming. This also ensures that the students do not come too close to the hot plate, the chemicals are not near the skin, and there is a constant distance for each trial.

Skin Contact

The acids (inorganic and organic) and alcohols may show irritation with contact to skin. Dropper bottles are used to minimize contact with skin, contamination, and odors in the laboratory.

Hazards

Sulfuric acid is corrosive and may cause burns. The organic acids (methanoic, ethanoic, 2-methylpentanoic, and *n*-butanoic acid) are irritants with prolonged exposure and may be corrosive in concentrated solutions. Alcohols (methanol, ethanol, 1-propanol, 2-propanol, and 1-pentanol) are flammable reagents that should be kept away from ignitable sources. 1-Pentanol is a lachrymator, causing irritation with prolonged exposure and in high concentrations. The potential harmful effects of the alcohols, carboxylic acids, and synthesized esters used in the laboratory have been minimized as they are used in minute quantities or diluted.

Results

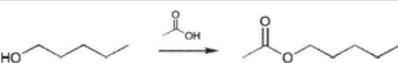
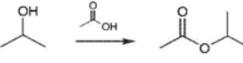
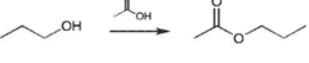
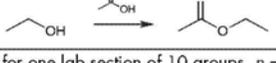
Esters synthesized were selected to allow for formation of distinct recognizable aromas. The alcohols and acids chosen

also allow for distinctive monitoring of the rates of formation. In Part A, students classified their synthesized esters with a wide range of descriptions (Table 1). In Part B, students explored structure-activity relationships and observed a general trend from the effects of increased chain lengths and steric bulk resulting in the increased time noted for emergence of the ester aroma (Table 2).

Part C entailed using the synthesis of ethyl acetate to examine how various factors affected the rate of the reaction. Students successfully determined that increasing the concentration of the carboxylic acid or the amount of the catalyst or alcohol added to the reaction decreases the time taken for the emergence of the ethyl acetate aroma since the reaction proceeds in the forward direction at a faster rate (Table 3). Students were able to observe the effect of the catalyst and discover it did not have a significant effect on the reaction after 10 drops of catalyst were added.

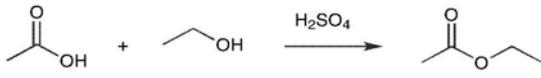
This experiment was designed as an inquiry-based experiment in which students were not explicitly told about expected trends but given general instructions and asked to study the results of the esterification reaction and provide conclusions. However, the students were prompted as to the time constraints and given guidance when necessary.

Table 2. Student Data on Effects of Alcohols for Part B

Reaction ^a	Time/s
	18 ± 3 (n = 2)
	29 ± 5 (n = 3)
	22 ± 3 (n = 3)
	17 ± 3 (n = 2)

^aData for one lab section of 10 groups, *n* = group.

Table 3. Data for Ethyl Acetate Aroma Detection by Varying the Amount of Ethanol and H₂SO₄ Catalyst

			
Drops of Alcohol	Time/s	Drops of H ₂ SO ₄	Time/s
1	56 ± 2	1	61 ± 2
2	46 ± 2	2	35 ± 2
5	39 ± 2	5	25 ± 3
7	35 ± 1	10	18 ± 2
10	32 ± 1	20	16 ± 2

NOTE: Data is from 4 groups.

Post-lab questions addressed chemical aspects of esterification kinetics. However, students did add their opinions about this experiment and we considered these relevant to the success of this experiment as a laboratory experience. Out of 15 students who gave informative non-solicited feedback about their experience in the lab, 8 students commented on how the experiments aided them in learning various aspects about the reaction studied, 7 commented on real-world applications such as aroma chemistry, 5 on the nose as an analytical tool, and 11 related to the experiment as a good learning experience. There were few negative comments asking for more time or stronger or weaker aromas. One of the students' comments summarizes the positive comments obtained: "I thought the experiment was good because being the measuring device was interesting. To know when it was happening without the fancy machines was nice. It also gave good insight into the different contributors to reaction speed, with noticeable changes which we measured."

Conclusions

This experiment utilized the sense of smell effectively allowing students to explore the synthesis of various esters and study the kinetics of these Fischer esterifications. Students synthesized a variety of esters, assigned them characteristic descriptions, and monitored the time it took for various esters to form. Students correlated this time to the structure of the reagents and explored factors that affect the formation of ethyl acetate as indicated by the development of the aroma. Specifically, the students were able to observe how trends in the size and branching of the starting reagents affected the rates of detection of aromas. These rates of detection were used to infer effects on the rate of the reaction. Students were also able to monitor the effect of the catalyst, amount of alcohol added, and concentration of the carboxylic acid.

Both individual and group data were used to rationalize the results and draw conclusions that were used to predict how long the synthesis of other esters would take based on observations and results from this experiment. Students monitored the characteristic aromas of the esters without the use of instrumentation or specialized equipment in an efficient and safe manner. In addition, students commented positively on the interest this new approach generated strongly supporting using the sense of smell to enhance this conventional organic laboratory and the chemistry experience in general.

Acknowledgments

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Literature Cited

1. Neppel, K.; Oliver-Hoyo, M. T.; Queen, C.; Reed, N. *J. Chem. Educ.* **2005**, *82*, 607–610.
2. Wood, J. T.; Eddy, R. *J. Chem. Educ.* **1996**, *73*, 257–258.
3. Flair, M.; Setzer, W. N. *J. Chem. Educ.* **1990**, *67*, 795–796.
4. Jones, G. M.; Andre, T.; Superfine, R.; Taylor, R. *J. Res. Sci. Teach.* **2003**, *40*, 303.
5. Ratliff, J. L. *J. Chem. Educ.* **1997**, *74*, 710–711.
6. Crosby, G. A. *J. Chem. Educ.* **1981**, *58*, 206–208.
7. Hiemenz, P. C.; Pfeiffer, E. *J. Chem. Educ.* **1972**, *49*, 263–265.
8. Tallman, D. E. *J. Chem. Educ.* **1978**, *55*, 605–606.
9. Anderson, J. L. *J. Chem. Educ.* **1982**, *59*, 871–872.
10. Cann, A.; Ross, D. *Am. J. Psychol.* **1989**, *102*, 91–102.
11. Chu, S.; Downes, J. *Mem. Cognit.* **2002**, *30*, 511–518.
12. Solomons, T. W. G.; Fryhle, C. B. *Organic Chemistry*, 7th ed.; John Wiley and Sons: New York, **2000**.
13. O'Lenick, A. J., Jr.; Parkinson, J. K. *J. Soc. Cosmet. Chem.* **1994**, *45*, 247–256.
14. Liu, Y.; Lotero, E.; Goodwin, J. *J. Catal.* **2006**, *243*, 221–228.
15. Huang, Y.; Sundmacher, K. *Int. J. Chem. Kinet.* **2007**, *39*, 245–253.
16. Kolah, A.; Asthana, N.; Vu, D.; Lira, C.; Miller, D. *Ind. Eng. Chem. Res.* **2007**, *46*, 3180–3187.
17. Gallaher, T.; Gaul, D.; Schreiner, S. *J. Chem. Educ.* **1996**, *73*, 465–467.
18. Birney, D. M.; Starnes, S. D. *J. Chem. Educ.* **1999**, *76*, 1560–1561.

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Full text (PDF) with links to cited JCE articles

Supplement

Experimental protocols for the students and detailed notes for the instructors including results and answers to post- and pre-lab questions

Appendix B . Qualitative Organic Analysis Experiment

Qualitative Organic Analysis Experiment and Post laboratory Questions

Introduction: Qualitative organic analysis is the identification of organic functional group(s) in a compound. Identification of compounds is an important aspect of chemistry, utilized in many industries such as drug discovery and research, proteomics, water quality testing and so on. In this experiment the physical and chemical properties will be explored to determine unknown functional groups. You should observe the physical appearance of your compounds as well as its odor. Some functional groups impart characteristic odors to its members. The sense of smell can be a powerful tool in identifying the functional group to which an unknown belongs. This can be used to your advantage by narrowing down chemical testing in order not to waste time and resources. The chemical tests used in this experiment are chemical reactions, which occur with the specific functional group, and gives products with different physical characteristics from the starting material. This makes it possible to watch the changes in smell, temperature, color, and sound. For students unable to view changes in color or intensity, a light probe may be used. The light probe can distinguish these changes by detecting changes in light passing through the test tube and emitting different frequencies or sound.

Prerequisites: A basic knowledge of organic functional groups. Students should review functional groups in their text books and make a table to bring to the lab. Prior to the lab, the hazards associated with this experiment should be researched and thoroughly discussed. For students using the light probe, consult the instructor.

Items needed:

Dropper bottles (samples and unknowns)	Deionized water
Solid sample vials	Spatula
Filter paper Strips (mostly small and a few large)	Hot plate
2% Potassium Permanganate solution (KMnO_4)	Test tubes, 10 cm (long) x 1.5 cm (diameter) or smaller
2,4-Dinitrophenylhydrazine Solution (2,4-DNP)	Test Tube rack
10% M NaOH	Acetone (for washing and dropper bottle)
Jones Reagent (Chromic acid)	Ethanol (dropper bottle)
Anhydrous Sodium Carbonate (Na_2CO_3)	Lumitest Light Probe
10% Hydroxylamine Hydrochloride	Ceric Ammonium Nitrate Solution (CAN)
Iron Nitrate ($\text{Fe}(\text{NO}_3)_3$) solution	Phenolphthalein Indicator
2.0 M HCl	Light probe

Warnings: All corrosive reagents used such as oxidants (CrO_3 , K_2MnO_4 , $\text{Fe}(\text{NO}_3)_3$ and CAN), strong acids and bases (HCl & NaOH) and acetyl chloride should be handled with proper care to avoid severe burns.

Jones', iron (III) nitrate, and ceric ammonium nitrate (CAN) reagents are oxidants and may cause fires in other compounds. Jones' reagent contains chromium which is toxic and carcinogenic. Flammable reagents should be kept away from ignitable sources. These include: alcohols (methanol, ethanol, and 2-propanol), ketones (acetone, methyl ethyl ketone and cyclohexanone), aldehydes (37% formaldehyde and diluted butyraldehyde), alkenes (cyclohexene and 1-hexene), and amines

(diethyl amine and propyl amine). Phenolphthalein and universal indicator solution contains alcohols hence potentially flammable. 2,4-Dinitrophenylhydrazine solution contains sulfuric acid and ethanol, so may be corrosive and flammable.

Extreme prolonged exposure to alcohols and ketones can be irritating to the skin and lungs. Methanol is toxic to the eyes. Excessive prolonged exposure to ethanamide and butanethiol may cause damage to the liver and kidneys. Wafting these chemicals is the only acceptable technique.

Strong aromas are perceived from aldehydes (37% formaldehyde and diluted butyraldehyde), and thiols (butanethiol and 1-octanethiol). Keep bottles tightly cap when not in use. 1-Octanethiol may be an irritant, may cause sensitization by skin contact, and allergic reactions.

Amines (diethyl amine and propyl amine) are incompatible with oxidizing agents, may cause burns (organic bases), and have strong odors which may cause burning sensation if inhaled directly. Sodium carbonate can be slightly irritating to some few students when inhaled, and the dust may cause coughing. Do not inhale this powder.

Consult instructor about chemicals spill and burns. Perform all experiments in the hood unless instructed to do otherwise. Instructor will demonstrate the proper way to smell compounds (wafting). Do not inhale the vapors for too long or directly from the bottle. Inhaling any compound too long or directly could be irritable and/or hazardous. Always waft aromas using the smelling strips provided.

Procedure:

Part A. Using your sense of smell to classify compounds: Locate your known samples and 20 strips of filter paper. Knowns F, G, L, O and P are located in the hoods. In your lab notebook, make a table such as Table 1, making sure all the samples are represented in the table. The smelling of the samples will be performed using filter paper strips. For liquids, place a drop of sample on the filter paper and note the smell by wafting. For solids, place a spatula tip of sample on a larger piece of filter paper and also observe the smell. As shown by the instructor, smell the compounds (**waft**) and record the odor (be creative), along with any other observations in the table. Once you have noted the smell, the paper may be placed in a waste beaker in the hood. Keep all bottles tightly closed when finished.

Place the compounds into groups according to your classifications. If you have trouble characterizing, first characterize into larger groups (such as pleasant and unpleasant). Go back through the groups and separate into similar odors. You must have between 7 and 9 groups (18 compounds).

Obtain a compound list with identifying letters from the instructor, and match your lettered samples with the compounds. Review the odors noted in your table for each functional group. Are your samples in the correct functional groups? If not, review the grouping according to the list given and repeat the smell test.

Part B. Testing your unknown: ALL TESTS MUST BE DONE IN THE HOOD. You will perform chemical tests in order to verify if the unknown was correctly placed (according to functional group smell). Note your unknown number to receive credit for your work. Classify your unknown as belonging to one of the groups determined in Part A. Only one group must be chosen and noted in your lab notebook. You may retest your known samples from Part A if you are unsure about the smells.

Ensure all equipment used including test tubes are clean and dry. From Table 2 determine the chemical tests needed to confirm the identity of your unknown functional group. Perform these characteristic tests as detailed in Table 3. Put a small amount of the solution or sample on a strip of filter paper, let dry for 10 seconds, and smell by wafting. Do not smell the test tubes directly.

Obtain your test reagents from your instructor and return them when finished so other groups may use them. Record all observations made in detail using your sense of smell, sight, touch and hearing. Use Table 4 as a guideline. Failure to record every observation may result in incorrect conclusions. Some chemical tests require different senses to discriminate between functional groups. It is essential that you use only the indicated results to confirm your unknown. You may compare two of your chosen tests with a known sample ONLY. Construct a chart that shows how you will conduct your experiments. Carefully look over Table 2 before starting, as you may use any test, but will be penalized for doing more than 2 tests. Plan your method carefully. If using light probe, consult instructor for the use before the lab.

Part C: Place all waste in the corresponding waste bottles as instructed. Rinse test tubes 3 times with small amounts of acetone over corresponding waste bottles before washing with soap in the sink. Clean up the workstation and return samples, unknowns and reagents to the instructor.

Table 1. Organic Compounds and Characteristic Odors Sample Table.

Compound	Grouped with	Odor	Actual Functional Group
A			
B			
C			
D			

Table 2. Characteristic Chemical Tests and Results.

Functional Group	Chemical Test	Definitive Results
Alcohol	Acetyl Chloride	Exothermic, a popping sound may be heard. Observe sweet fruity smell.
	Ceric ammonium Nitrate (CAN)	Observe deep red-brown solution. *Light probe: Decrease in the frequency observed.
Aldehyde	Jones Reagent	Exothermic, change in smell. No color changes with NaOH. *Light probe: little or no sound.
	Baeyer's Reagent	Brown precipitate forms. *Light probe: Frequency of sample should decrease or no sound heard.
Carboxylic Acid	Na ₂ CO ₃	Fizzing sound (gas given off).
	pH - acidic	Solution becomes warm and has no smell detected. Indicator turns from green to red. *Light probe: Increased frequency, compared to pure indicator.
Amine	pH - basic	Solution gets warm and no smell detected. Indicator turns from clear to pink. *Light probe: Decrease in frequency should be heard.
	Acetyl Chloride	Exothermic, a popping sound may be heard, solid formed, amide smell observed.

Table 2. Characteristic Chemical Tests and Results (continued).

Functional Group	Chemical Test	Definitive Results
Ketone	2,4-DNP	Yellow or orange solid forms with different smell from the ketone. *Light probe: A decrease in the intensity of the frequency.
Thiol	Jones Reagent	A mixture of a sweet and stench smell noted. Observe dark brown solution. *Light probe: A decrease in the intensity of the frequency.
	Baeyer's Reagent	Brown precipitate forms, and mixture of a sweet and stench smell. Solution turns green to light brown with NaOH. Precipitate becomes more obvious. *Light probe: Frequency of sample should decrease or no sound heard.
Alkene	Baeyer's Reagent	Solution forms a brown precipitate. Solution turns dark green back to brown with NaOH. Solution has a sweeter smell than original compound. *Light probe: A decrease in the intensity of the frequency.
Ester	Ferric hydroxamate test	A burgundy or magenta solution should be observed (no precipitate). *Light probe: No sound should be observed with a darkened solution.
Amide	Hydrolysis	Ammonia odor is detected.
	Acetyl Chloride	Exothermic. White cloudy solution/ precipitate formed, becomes thick yellow water soluble precipitate, within 10 minutes. *Light probe: A low frequency sound should be observed.

Table 3. Chemical Test Procedures.

Chemical Test	Procedure (performed in test tubes):
Acetyl Chloride	To 10 drops of liquid, add 10 drops of acetyl chloride slowly. Gently shake. Add acetyl chloride very cautiously and allow each drop to react before adding the next drop. Allow the excess acetyl chloride to evaporate in the hood for a few minutes before smelling.
Ceric ammonium Nitrate (CAN)	To 10 drops of liquid, add 5 drops of the CAN reagent and gently shake. *Light probe: Position the light probe in order to observe frequency changes with reagent addition.

Table 3. Chemical Test Procedures (continued).

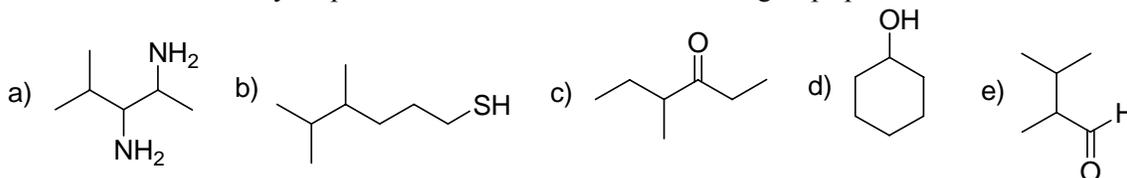
Chemical Test	Procedure (performed in test tubes):
Jones Reagent	<p>To 10 drops of acetone, add 5 drops sample then carefully add 5 drops of the reagent. Shake gently. Note the immediate changes. A deep blue or blue green solution should form.</p> <p>*Light probe: Position the light probe in order to observe frequency changes with addition of the reagent. If unable to distinguish, make a standard for comparison, using 15 drops of acetone.</p>
Na_2CO_3	<p>To 10 drops of liquid, add 10 drops of deionized water. Add a spatula tip of Na_2CO_3, and listen.</p>
pH - Acidic	<p>To 10 drops of liquid, add 10 drops of deionized water. Add 1 drop of universal indicator, and shake. To another 5 drops of liquid or a spatula tip of solid, add 10 drops of 10% NaOH.</p> <p>*Light probe: Position the light probe in order to observe frequency changes. Standards may be set-up using HCl and NaOH with the indicator.</p>
pH - Basic	<p>To 5 drops of liquid, add 10 drops of deionized water. Add 2 drops of phenolphthalein, and shake. To another 5 drops of liquid, add 15 drops of 2.0 M HCl.</p> <p>*Light probe: Position the light probe in order to observe frequency changes. Standards may be set-up using HCl and NaOH with the indicator.</p>
2,4-DNP	<p>To 10 drops of ethanol with 10 drops of your sample, add 15 drops of the reagent are added. Shake vigorously. A yellow to red-orange solid forms. The solid should have a different smell from the ketone. Place a small amount of the solid on filter paper, and smell after a few minutes.</p> <p>*Light probe: The light probe is positioned in front of the test tube.</p>
Baeyer's Reagent	<p>To 5 drops of liquid, add 10 drops deionized water. Add one drop of the Baeyer's reagent and shake vigorously. Add 20 drops of 10% NaOH dropwise and shake. Note any changes with each drop.</p> <p>*Light probe: In another tube, place 20 drops of water and a drop of the Baeyer's reagent. Compare this with your sample.</p>
Ferric hydroxamate test	<p>Boil a mixture of 5 drops of sample, 10 drops of hydroxylamine hydrochloride, 20 drops of ethanol and 5 drops of 10% NaOH solution for 5 minutes. Cool for a few minutes. Slowly add 10 drops of 2 M HCl, if the solution turns cloudy add 10 drops of ethanol. Add one drop of ferric nitrate.</p> <p>*Light probe: Position the light probe in order to observe frequency changes.</p>
Hydrolysis	<p>To 10 drops of sample, add 20 drops 10% NaOH and warm to $\sim 50\text{-}60^\circ\text{C}$. For this test, waft the test tube.</p>

Table 4. Sample Table for Results of Chemical Tests.

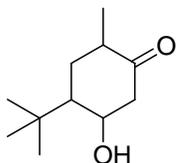
Unknown #	Test	Results
	Initial Smell	Smell: Guessed Functional Group:
		Smell: See: Touch: Hear:

Level – First semester organic chemistry questions:

- 1) Give your rationale for your choice in confirmatory tests?
- 2) Given the following structures, what would you expect the compounds to smell like? Determine what chemical tests may be performed to confirm the functional groups present. Give details.

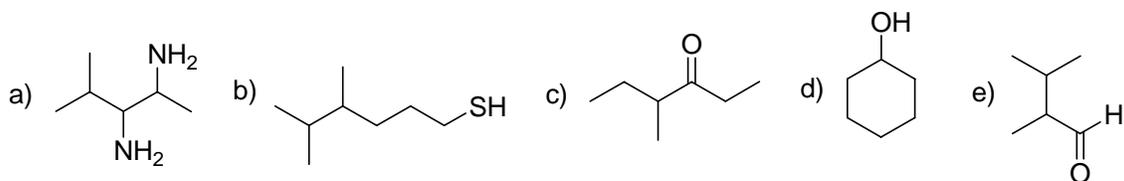


- 3) What did you learn from this lab about functional groups?
- 4) Where else in your life or environment have you observed these functional groups? Specifically, where have you noticed similar smelling compounds?
- 5) What chemical tests may be used to identify the functional groups in the following compound? What results would you expect from each test?



Level – Second Semester Organic Chemistry questions:

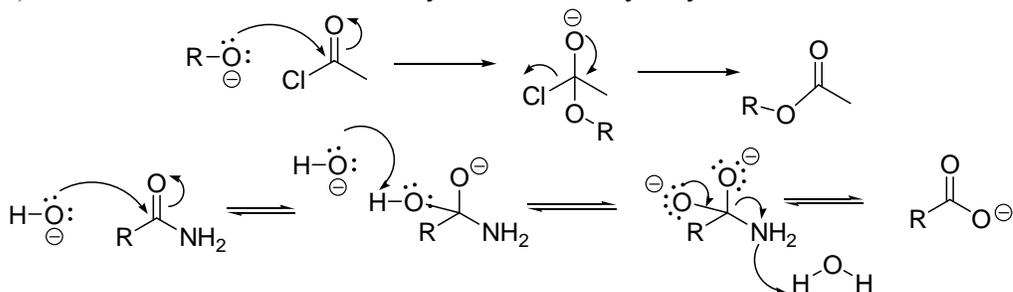
- 1) Give your rationale for your choice in confirmatory tests?
- 2) Given the following structures, what would you expect the compounds to smell like? Determine what chemical tests may be performed to confirm the functional groups present. Give details.



Given that the Jones reagent oxidizes aldehydes, what is the product of the reaction? Considering the Jones reagent contains sulfuric acid and chromium trioxide, could you chemically test for the product without purification using only the chemical test for this functional group?

3) If you were told that the product of the reaction with acetyl chloride and an alcohol gives an ester, propose a mechanism.

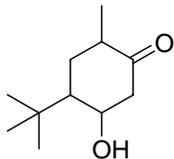
4) What is the role of the sodium hydroxide in the hydrolysis of amides?



5) How can this lab be applied to real world situations?

6) Where else in your life or environment have you observed these functional groups? Specifically, where have you noticed similar smelling compounds?

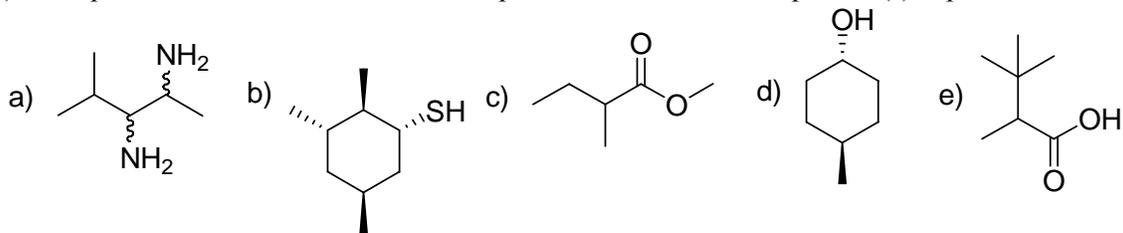
7) What chemical tests may be used to identify the functional groups in the following compound? What results would you expect from each test?



Level - Advanced Organic Chemistry questions:

1) Give your rationale for your choice in confirmatory tests?

2) Propose a mechanism of the reactions performed as well as the product(s) expected?



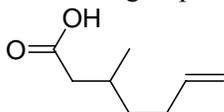
3) Given the following structures, what would you expect the compounds to smell like? Determine what chemical tests may be performed to confirm the functional groups present. Give details.

4) What other ways can you determine the identity of your unknown(s)? Be very specific and given details.

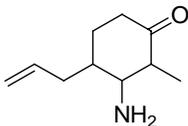
5) How can this lab be applied to real world situations?

6) Where else in your life or environment have you observed these functional groups? Specifically, where have you noticed similar smelling compounds?

7) Given the following structure, determine what chemical tests can be performed to determine the functional groups? What other ways can the functional groups can be identified? Give details.



8) Given the following structure, determine what chemical tests can be performed to determine the functional groups? If all the functional groups present can not be positively identified, given full details on how else the functional groups can be identified?



Pre-Laboratory Question: Functional groups –For each of the following functional groups, look up the functional group structure, give at least one example of that group, and any characteristics about this group. Make a table and bring to the laboratory.

alcohol

alkane

alkyne

amine

ester

aldehyde

alkene

amide

ketone

thiol

Qualitative Organic Analysis Instructor's Notes

Purpose: To identify functional groups using the senses of smell, sight, hearing and touch. Basic functional groups will be classified according to characteristic smells. Based on these classifications, an unknown will be classified. In order to prove that the compound is a member of the chosen functional group, chemical tests will be performed to positively identify the unknown compounds.

Reagents used (CAS numbers)

Potassium permanganate - 7722-64-7	Acetone - 67-64-1
2,4-Dinitrophenylhydrazine - 119-26-6	Propyl amine - 107-10-8
Sodium hydroxide - 1310-73-2	Ethyl acetate - 141-78-6
Chromium oxide - 1333-82-0	Acetyl chloride - 75-36-5
Nitric acid - 7697-37-2	Methanol - 67-56-1
Hydrochloric acid - 7647-01-0	Ethanol - 64-17-5
Sulfuric acid - 7664-93-9	2-Propanol - 67-63-0
10% Hydroxylamine hydrochloride - 5470-11-1 (in water CAS 7732-18-5)	37% Formaldehyde - 50-00-0
Iron III nitrate - 10421-48-4	Cyclohexanone - 108-94-1
Diethyl amine - 109-89-7	Cyclohexene - 110-83-8
<i>N</i> -methylacetamide - 79-16-3	Butyraldehyde - 123-72-8
Citric Acid - 77-92-9	Methyl ethyl ketone - 78-93-3
Ceric ammonium nitrate - 16774-21-3	1-hexene - 592-41-6
Phenolphthalein Indicator - 77-09-8	1-Octanethiol - 111-88-6
Ethanamide - 60-35-5	<i>n</i> -Propyl acetate - 109-60-4
Lumitest light probe - American Printing House for the Blind Inc., Louisville KY.	Sodium Carbonate - 497-19-8
	Ceric Ammonium Nitrate - 16774-21-3
	Vinegar (acetic acid)
	Universal Indicator

Directions for making reagents:

Baeyer's reagent: To 4.0 g of potassium permanganate crystals are added 196.0 mL of deionized water. Place the solution in a dark bottle and allow to sit overnight. If the solution turns cloudy, filter to remove solid and place in a clean dark bottle.

2,4-Dinitrophenylhydrazine solution: 2.4 g of 2,4-dinitrophenylhydrazine is dissolved in 12.0 mL concentrated sulfuric acid. Add 16.0 mL of deionized water and 56.0 mL 95% ethanol with stirring and place in a clean bottle when cooled. If the solution turns cloudy, filter solution into a clean reagent bottle.

2.0 M Hydrochloric acid: In a volumetric flask, add slowly 33.3 mL conc. Hydrochloric acid to 100.0 mL of deionized water. Swirl the solution slightly, and add more deionized water (66.7 mL) to fill the flask to the mark. The solution is shaken to completely mix.

10% Sodium Hydroxide: To 5 g of sodium hydroxide pellets, add 45 mL deionized water. The solution is shaken to allow all the pellets to dissolve.

Jones Reagent: In an ice bath at about 0-5°C, 22.0 g of chromium oxide is added to 42.0 mL deionized water and to this solution 17.0 mL of concentrated sulfuric acid is added. Additional deionized water is added until the solute is all dissolved (not more than 33 mL).

5% Iron III Nitrate solution: 1 g of iron nitrate is placed in 19 mL of deionized water. The solution is shaken until the solid dissolves.

Ceric ammonium nitrate solution: 40 g of Ceric ammonium nitrate is placed in 88 mL of deionized water. To this solution, 13 mL Nitric acid is added, with stirring.

50% Citric Acid solution (unknown 6): 20 g of citric acid is placed in 20 mL deionized water. The solution was stirred until all of the solid dissolved.

Phenolphthalein solution: 0.05 g of phenolphthalein is placed in 50 mL of deionized water. To this solution, 50 mL of ethanol is added.

Butanethiol known solution: 1 mL butanethiol was placed in a dropper bottle. 10 mL of cold deionized water was added along with 10mL of ethanol. The solution was capped and shaken thoroughly.

Butanethiol unknown solution: 2 mL butanethiol was placed in a dropper bottle. 10 mL of cold deionized water along with 1mL of ethanol. The solution was capped and shaken thoroughly

Butyraldehyde known solution: 5 mL butyraldehyde was placed in a dropper bottle. 10 mL of cold deionized water was added along with 10mL of ethanol. The solution was capped and shaken thoroughly.

All reagents containing acid can be placed in glass dropper bottles and other reagents may be placed in plastic dropper bottles. The dropper bottles are used to reduce contamination of the reagents. The bottles should be kept closed to keep the solutions. Nitrous Acid bottle should be kept in an ice bath at all times (replenishing the bath as needed).

Hazards.

The use of strong acids and bases may cause burns and be corrosive. Acetyl chloride will burn the skin, nose irritant and is corrosive. Caution should be taken when adding acetyl chloride to samples, as it may splash if the reaction gets too hot. It should be added very slowly, waiting for reaction to stop bubbling/popping before adding more acetyl chloride. Potassium permanganate and chromium oxide reagent may stain skin. Iron III Nitrate, Ceric Ammonium Nitrate Potassium permanganate, and chromium oxide are oxidants, and are flammable. Chromium oxide is known to be toxic and carcinogenic. Students should wash their hands thoroughly with soap after the lab, as some organic chemicals do not wash away with water. 2,4-Dinitrophenylhydrazine is flammable when dry. Extreme prolonged exposure to the skin and lungs may cause cyanosis. 10% Hydroxylamine hydrochloride may cause irritation to eyes and skin, corrosive, and poisonous. Amides (Ethanamide and *N*-methylacetamide) may be irritating. Ethanamide is hygroscopic and excessive prolonged exposure may cause damage to the liver.

Alcohols (Methanol, Ethanol, and 2-Propanol) are flammable and extreme prolonged exposure can be irritating to the skin and lungs. Methanol is toxic to the eyes. Ketones (Acetone, Methyl ethyl ketone and Cyclohexanone) are flammable and extreme prolonged exposure can be irritating to the skin and lungs. Alkene (Cyclohexene and 1-hexene) are flammable and excessive

prolonged exposure can be irritating to some students. Butanethiol is an irritant, extreme prolonged exposure may be toxic to the liver and kidneys, flammable, and has very strong odor. Sodium carbonate can be slightly irritating to some few students when inhaled, and the dust may cause some students to cough. Do not inhale this powder. Aldehydes (37% Formaldehyde and diluted Butyraldehyde) may be irritants, flammable and have a strong odor. 1-Octanethiol may be an irritant, may cause sensitization by skin contact, allergic reactions and has a strong odor. Amines (Diethyl amine and Propyl amine) flammable, incompatible with oxidizing agents, may cause burns (organic bases), strong odors which may cause burning sensation if inhaled directly.

Suggestions and Notes

- Demonstrate to students how to smell the chemicals. Students should not directly inhale from the test tube. Student should place all samples on filter paper before smelling. Wafting should be demonstrated. Instruct the students to be even more cautious with the unknowns.
- Coffee crystals can be made available for the students to smell between compound identification. This is a recommended procedure to “clean” the sense of smell. Some students took advantage of this while others didn’t think it was necessary.
- Table B.1 should be given or made available to students only after they have made their sample groups. Table 6 should not be given to the students.
- Students are given 18 known samples, which are identified by letters. Students are given 1 unknown sample, identified by a number they must record to receive credit.
- All unknowns are liquid or made into liquid sample. The sense of smell is only used to predict functional groups.
- Make clear to the students that only the indicated positive results should be used as evidence for a particular functional group. Other results may occur, especially with other functional groups, so it is essential that students use the table for analysis. All observations should be recorded.
- Make sure students do not perform all the tests in Table 2. The instructor should limit the use of reagents and excessive testing should be penalized. The basis of this experiment is for the students to use the sense of smell as a discriminating tool for identifying functional groups. The students can then use chemical tests to confirm their findings. These tests employ different senses to discriminate between various groups. For students at a more advanced level (second semester of organic or advanced organic).
- Mechanisms and products of these chemical tests can be determined from their knowledge of organic reactions.
- For students using the light probe, have them familiarize themselves with how the probe works and the different frequencies it emits. Have a variety of test tubes set-up with a range of colors from clear to opaque, so the students can spend a couple of minutes using these probes and familiarize themselves with the sounds. Have the light probe instructions available to the student, before and during the lab.
- Have students work in groups of two or three maximum.
- The questions posted to students are grouped in terms of the academic level. The questions above or below the students level should be removed.
- This lab may be complimented with spectroscopic methods.
- Have several waste containers available for the students. Bottles for manganese, chromium, and general organic.
- Other confirmatory tests maybe used such as the Iodoform and Lucas tests, however, these require on the sense of sight or the use of the light probe. The aromas generated from these tests are difficult to distinguish from the test reagents.

- In order to reduce the odors in the laboratory, use octanethiol or any less smelly thiol. Thiols were given to students closest to the large fume hoods.
- Butanethiol was diluted using water and ethanol. The thiol odor dominated, but was reduced significantly and not as obnoxious. Diethyl ether can be used instead of ether to help dissolve the thiol, but ethers are known to be more flammable than alcohols and can be potentially explosive.
- The butyraldehyde sample used in Part A was diluted in order to prevent the laboratory from smelling, as this sample would be opened frequently compared to the unknown.
- The fume hoods on each student's work station were turned on during the entire experiment. This may make hearing the light probe difficult. Our students used the instrument room to use the light probe, as it was quiet enough to hear the sounds.
- Other carboxylic acids such as butyric acid, trimethyl acetic acid and dimethyl acid may be used when diluted in water.

Table B.1. List of Organic Samples/Functional Group and Corresponding Numbers/Letters.

Compound	Functional Group	Compound Name
A	Alcohol	Methanol
B	Amide	Ethanamide
C	Aldehyde	Formaldehyde
D	Ketone	Cyclohexanone
E	Carboxylic Acid	Acetic Acid
F	Amine	Butylamine
G	Thiol	Butanethiol
H	Alkene	Hexene
I	Ester	<i>n</i> -Propyl acetate
J	Alcohol	Ethanol
K	Amide	<i>N</i> -methylacetamide
L	Aldehyde	Butyraldehyde
M	Ketone	Acetone
N	Carboxylic Acid	Citric Acid
O	Amine	Diethyl amine
P	Thiol	1-Octanethiol
Q	Alkene	Cyclohexene
R	Ester	Ethyl acetate

Table B.2. List of Unknowns.

Unknowns	Functional Group	Compound Name
1	Alcohol	2-Propanol
2	Ketone	Methyl ethyl ketone
3	Thiol	Octanethiol
4	Alkene	Cyclohexene
5	Aldehyde	Butyraldehyde
6	Carboxylic Acid	50% Citric Acid Solution
7	Amine	Propylamine
8	Amide	<i>N</i> -methylacetamide
9	Ester	Ethyl acetate

Table B.3 may be given to the students, however, it is strongly suggested that students make up their own descriptions and categories. You may also advise students that they do not need to have the same descriptive words as their peers. Their descriptions of odor are relatively subjective, just as color is relatively subjective. This experiment is intended to be inquiry-based, therefore the students are given only what is needed to perform the experiment. They must decide for themselves what would best describe the smells they observe. By doing this, they may also be more inclined to remember the functional groups and link them to descriptions to which they are familiar.

Table B.3. Examples of descriptive words to be used describe the smells of the samples.

Functional Group	Smells	Compounds
Alcohol	Rubbing alcohol, drinking alcohol, clean smell	Methanol, Ethanol, t-Butanol, 1-Propanol, 2-Propanol
Amide	Wet animal, animal-like	Ethanamide, N-methylacetamide
Aldehyde	New house smell, preservative, sharp, irritating	Formaldehyde, butyraldehyde
Ketone	Sweet, nail polish remover, paint thinner	Cyclohexanone, Acetone
Carboxylic Acid	Vinegar, sour, sharp	Acetic Acid, Citric acid
Amine	Ammonia like, sharp, irritating	Butyl amine, Diethyl amine
Thiol	Skunk-like, burnt rubber, acrid, pungent	Butanethiol, Octanethiol
Alkene	Oil, oil refinery, gasoline like	Hexene, cyclohexene
Ester	Fruity, sweet, perfume	Ethyl acetate, n-Propyl acetate

Table B.4. All student responses aroma classifications.

Compound	Compound Name	Students
A	Methanol	Bananas, weak pinsol, sweet, really light smell, odorless, fruit-like, faintly sweet, sweet alcohol, rubbing alcohol, wet paint, sweet citrus smell, onions, clean, orange, fresh dirt, burnt food, finger nail polish, the sweetness, wet feet, faint citrus, somewhat of an alcohol,
B	Ethanamide	Dirty dog, glue, no smell, feet, none, nothing, sharp sour, faint smelly feet, sweat, body odor, sweet, mothball-like, melted plastic, a bit eggy, plasticity, plastic, rubber, eggs, ointment, acidic, old person's house, glue, dirty animal, burning plastic, weak coffee [maybe contaminated from coffee], ammonia like, dog in need of a bath, faint burnt plastic, wet dog with vinegar, melted plastic, bad, bitter smell, old book,
C	Formaldehyde	Almond, sesame oil, earthy, dirty dog, permanent marker, fritos chips, latex paint, finger nail polish, magic marker, paint thinner, rubbing alcohol, nutty sharp, marker, ink, sharp, sesame oil like, peroxide, Target/dull, unpleasant, burning alcohol, moel glue, aerosol glue, after effect nostril burning, weak pinsol, dirty dog, acetone, alcohol smell, faint citrus, rubber cement,

Table B.4. All student responses aroma classifications (continued).

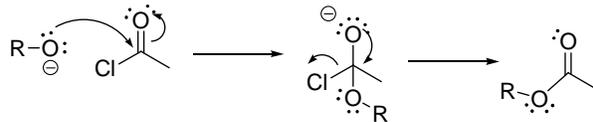
Compound	Compound Name	Students
D	<i>Cyclohexanone</i>	Soap in public bathrooms, peppermint, Doctor's office, sweet, odorless, raspberry, marker like, touch of mint, bathroom cleaner, peppermint, new car smell, rotten fruit, rubber cement, cherry cough drops, cleaning liquid, like chocolate, rubber cement, air inside a new package/plastic, new beach ball, strong alcohol, cleaning stuff maybe bleach, acetone + rotten fruit, acetone, fruity alcohol, paint thinner, cough medicine,
E	<i>Acetic Acid</i>	Vinegar, sour vinegar, glue, really bad, rotten feet, nursing home, elmer's glue, permanent markers, urinal tablet, rubber cement, dusty,
F	<i>Butylamine</i>	Bleachy, chlorine, horse urine, hair perm, urine, fishy smell, ammonia, tuna, stink bait, rotten fish, garbage, car oil, formaldehyde, pool chemical storage room, chlorine, bleachy ammonia, stinky,
G	<i>Butanethiol</i>	Sulfur rotten eggs, really bad garlic, rotten/burnt pumpkin seeds, awful burnt car, sweetener, old tire, burning plastic, x82, burnt popcorn, bad car fumes, onions, garlic, rotting bad smelling onions, bad sulfur, stinky dog poop, burnt pumpkin seeds, raw onion, bad dog poo, rotten nasty bitter, awful dog sh*t bad,
H	<i>Hexene</i>	Unique chemical smell, cheap fruity perfume, nail salon, acrylic nails, glue, alcohol, paint thinner, rotten veggies, chlorine, rubber, nail salon that has not been cleaned, a latex glove in a swamp, gasoline, onion, hot copier ink smell, badness, moldy stuff, very unpleasant, rubber brand, gas + glue, unleaded gas + glue, rotten cabbage,
I	<i>n</i> -Propyl acetate	Permanent marker, glue, onion, super glue, like acetone, finger nail polish, glue, mineral spirits, paint thinner, acetone, finger nail polish remover, fruity,
J	Ethanol	Everclear, disposable lab gloves, latex, rubber gloves, elmer's glue, sweet, faint hair product (dye), fruity, stingy, new shoes – leather and rubber, gin, latex gloves, aquarium water, cleaner, vodka, fruity beer, super glue, chlorox, weak pinsol/chlorox, sweet alcohol, faint alcohol,
K	<i>N</i> -methylacetamide	Bitter, dirty diaper, stinky boys locker room, BO [body odor], hot eraser, stuffed animal, used eraser, rubber eraser, paper, nursing home, old people, stinky rose, rotten flower, weak gasoline, faint bitter odor, musty wet animal, stinky boy, old, musty, burnt smell, strong dusty/garbage, rotten,
L	Butyraldehyde	Like vomit, fried plantains, puke, throw-up, old stale crackers, burning playdoh, rotten wood, rotten, salty butter, cheese sauce, sweet flowers, burnt clay, sweet stink, fake cheese, old stale crackers, very bad, highlighter, sulfur and butt, sweat stink/unpleasant, strong permanent marker, sweaty nasty stank,

Table B.4. All student responses aroma classifications (continued).

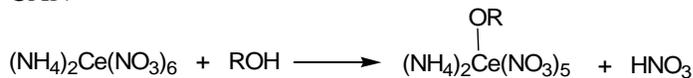
Compound	Compound Name	Students
M	Acetone	Moldy moth-balls, acetone, store abrasive smell, banana, weak alcohol, paint thinner, permanent marker, plastic, cheap vodka, rubber cement, mild acetone, solid nailpolish,
N	Citric Acid	Cheese, salty, really weak light clean smell, odorless, crayon, waxy, none, weak acid, burning tires, plastic, salt, stale, unpleasant, new plastic, salty, musty, musty old attic, faint cheese, faint sour, salty, hay,
O	Diethyl amine	Chlorine smell, bad musty smell, musty, dead animal, urine, something dead, heavy duty cleaner, 'ass', smells like awful ammonia, like chlorox cleaner, bleach, very rotten fish, ammonia, household cleaner, pee, rubbing alcohol, very harsh chlorine, good god what are you doing to me, Doe in heat "Buck attractant", animal musk, bad, old antifreeze, alcohol + fish, bad,
P	1-Octanethiol	Sweet burning rubber, bad chips, flower smell, woody smell, like pine, construction tar, cardboard, burnt clutch, burning rubber in a field of flowers, hornet killer, hot rubber, burning rubber, onion/garlic/chive, skunk, combo, burnt rubber, fruity and rubbery, bad potato chips, pee, fermenting vegetable/chips, burning/fruity, sweet but something is burning, strong grass, burnt copper,
Q	Cyclohexene	Citrus pledge, badness, car exhaust, bitter sour, really bad, sour bitter, vinegar, pine, burning rubber, kerosene, fuel, gas-like, foul, paint thinner, vinyl, nail salon on crack/glue, mint, burning legos, permanent marker, engine/car fumes, department store, exhaust, mint, burning brakes, diesel, rubber cement, gasoline station, bad rotting vegetables, strong badness, burning bubble gum on top of a dead animal or glue, displeasent, death, undesirable, rotten,
R	Ethyl acetate	Acetone, rubber cement, acetonish, finger nail polish remover, thinner, acidic, sharp, stingy, reminding of salicylic acid, rubbing alcohol, permanent marker, vinegar, burnt rubber, industrial strength ammonia, in between J [ethanol] and M [acetone], nail polish, strong crap/ammonia, rubber cement + cigarettes, glue,

Proposed Mechanisms and Products Formed

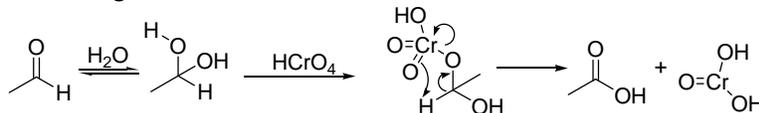
Alcohol Acetyl Chloride - Nucleophilic substitution



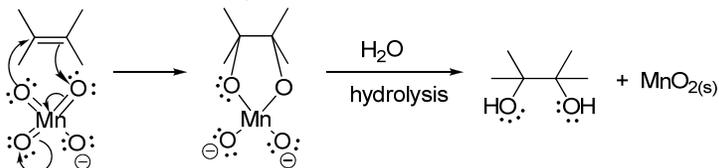
CAN



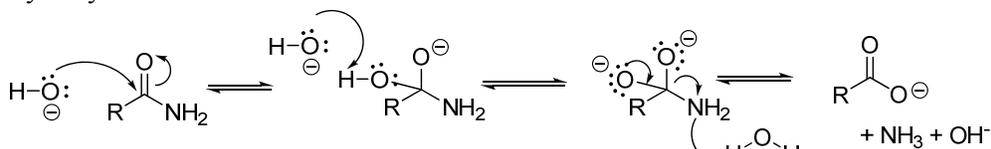
Aldehyde Jones reagent - oxidation



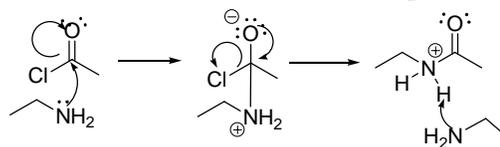
Alkene



Amide Hydrolysis of Amide

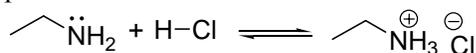


Amine

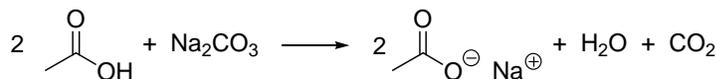


Nucleophilic substitution

pH test



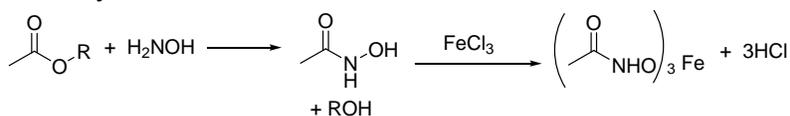
Carboxylic Acid Sodium Carbonate Test:



pH test

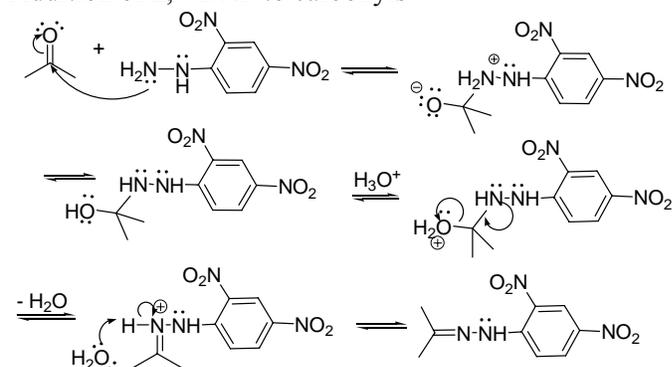
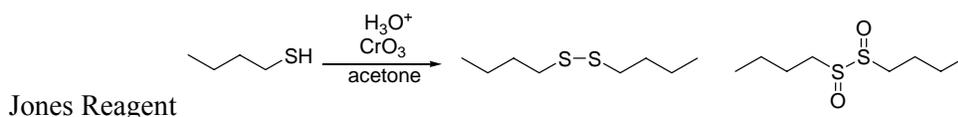


Ester Ferric hydroxamate test



Ketone

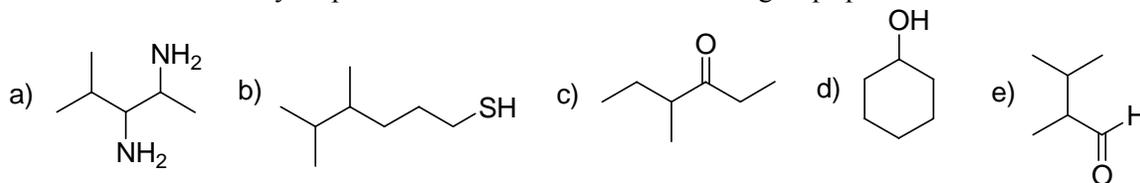
Addition of 2,4-DNP to carbonyls

**Thiol****Rubric, Questions and Answers, and Additional student data****First semester organic Chemistry:**

1) Give your rationale for your choice in confirmatory tests?

Answer: This question depends on the chemical tests performed. The student should explain that they characterized the compound into one of the functional groups according to its smell. Then they should be able to show that their results prove or disprove their idea. If not, the student should immediately perform another experiment to determine the functional group. This requires the students to think about the tests, and if multiple functional groups can be tested for with the same reagent, this may be a good place for the student to start. Based on the smell, the student can devise a testing chart.

2) Given the following structures, what would you expect the compounds to smell like? Determine what chemical tests may be performed to confirm the functional groups present. Give details.



Answer: Students can use any of the tests indicated in Table 2 with results to justify their answer. a) Ammonia-like smell., b) Skunk-like., c) Sweet, acetone-like., d) Alcohol-like, clean., e) Sharp, irritating.

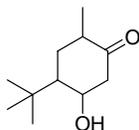
3) What did you learn from this lab about functional groups?

Answer: The student may state that functional groups can be characterized by physical and chemical properties. The use of multiple senses can be helpful in identifying an unknown.

4) Where else in your life or environment have you observed these functional groups? Specifically, where have you noticed similar smelling compounds?

Answer: The student should be able to give a couple examples. For example: acetic acid – in vinegar, amines – in ammonia, ester – in fruits, carbonyl- in nail polish remover or thinner, alkenes – in oil or gasoline.

- 5) What chemical tests may be used to identify the functional groups in the following compound? What results would you expect from each test?



Answer: The student may use acetyl chloride and CAN to test for alcohol. This test would result in a sweet smell as an ester forms. The ketone may be verified by testing 2, 4-DNP, which would result in a yellow solid differing in smell from the ketone.

Table B.5. Rubric for qualitative organic experiment (Section 203).

Section	Criteria	Points
<i>Pre-lab</i>	Provide each Functional group structure	10
	Provide each Functional group example	5
	Any characteristic of each functional group	5
<i>Knowns</i>	Table of known smells(18)	18
	Students groupings (reasonable)	9
<i>Unknown</i>	State unknown number	1
	Unknown smell	2
	'Guessed' functional group	2
<i>Chemical Test</i>	Tests performed, limited to 2 without penalty.	2
	Completion of test (performed entire test and recorded all information).	1
	Result	5
<i>Questions</i>	1. Rationale for test(s).	5
	2. 3 points each, 1 for smell, 1 for test, 1 for details	15
	3. individual based, should relate to functional group smells	2
	4. 1 point per functional group, 1 point extra credit	8
	5. 1 point for each test, 4 points for each result	10

Rubric was modified based on experiences with this pilot section (as described in Section 3.2). This was the first section to perform the experiment. Many did not do the pre-lab done or read the experiment prior to the lab.

Table B.6. Rubric for qualitative organic experiment (Sections 202, 204 and 206).

Section	Notes	Points
<i>Pre-lab</i>	Provide each Functional group structure	10
	Provide each Functional group example	5
	Any characteristic of each functional group	5
<i>Knowns</i>	Table of known smells(18), use of table in lab	9
	Students grouping, correction of grouping	7
<i>Unknown</i>	State unknown number	1
	Unknown smell	2
	'Guessed' functional group	2
<i>Chemical Test</i>	Tests performed (1-2 tests, -1 for each addition test)	2
	Completion of test (do entire test, including light probe portions)	2
	Results (see, hear, smell, touch)	5
<i>Procedure</i>	Brief procedure – how lab was performed.	5
<i>Conclusion</i>	Brief Conclusion based on work done in lab.	5
<i>Questions</i>	1. Should be based on the smell of unknown, rationalize tests	5
	2. 3 points each, 1 for smell, 1 for test, 1 for details	15
	3. individual based, should relate to functional group smells	2
	4. points awarded for examination of functional groups and smells	6
	5. 2 points for each functional group identified, 2 points for correct test for each, 8 points for correct expected results (complete).	12

Table B.7. Grade percentage ranges with the percentage of total student, male (m) and female (f) by lab section.

	All	m	f		All	m	f		All	m	f		All	m	f
Grade range	204				203				206				202		
40-49%	12	12	0		0	0	0		0	0	0		0	0	0
50-59%	0	0	0		0	0	0		0	0	0		11	2	0
60-69%	6	0	6		10	10	0		5	1	0		17	1	2
70-79%	18	18	0		60	50	10		15	2	1		22	2	2
80-89%	29	18	11		20	20	0		45	5	4		28	3	2
90-100%	29	11	18		10	10	0		25	3	2		22	0	4
100%-	6	6	0		0	0	0		10	1	1		0	0	0
# of students	100	65	35		100	90	10		100	12	8		100	8	10

Table B.8. Number of students with complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N) and average percentages for pre and post lab questions.

	Section 203					Sections 202, 204, 206				
	Average	C&C	C	SC	N	Average	C&C	C	SC	N
FG structures	82%	8	1	0	1	95%	50	3	0	2
example	87%	9	0	0	1	70%	48	0	0	7
characteristic of FGs	50%	5	0	0	5	0%	0	0	0	55
known smells(18)	98%	10	0	0	0	100%	55	0	0	0
grouping	90%	10	0	0	0	100%	55	0	0	0
State unknown number	100%	10	0	0	0	100%	55	0	0	0
Smell	75%	7	1	0	2	55%	18	12	0	25
functional group	70%	7	0	0	3	80%	36	5	0	14
Tests done	55%	4	3	0	3	70%	45	5	0	5
Completion of test	40%	4	0	0	6	60%	32	8	0	15
Results	70%	7	0	0	3	88%	50	2	1	2
1	84%	8	0	2	0	74%	44	4	3	4
2	44%	0	6	4	0	73%	15	26	11	3
3	100%	10	0	0	0	90%	52	1	0	2
4	60%	4	4	2	0	53%	23	20	4	8
5	63%	4	3	1	2	63%	40	3	7	5
Brief procedure	Not required.					30%	21	0	0	34
Brief Conclusion						50%	19	4	1	31

Appendix C. Esterification Kinetics Experiment

Esterification Kinetics Experimental Procedure and Pre and Post laboratory Questions

Introduction: Low molecular weight esters generally have pleasant aromas. These aromas typically resemble fruits, and are used in synthetic flavoring. A common method for the synthesis of esters employs a carboxylic acid and an alcohol with a concentrated mineral acid to catalyze the reaction (Fischer esterification). Various factors affect the rate of the esterification reaction. These factors can be studied by observing how long it takes for the aroma of the ester to emerge.

Pre-lab: Review the functional groups used in this experiment (carboxylic acids, alcohols and esters) with respective nomenclature, structure and properties. Write a generic mechanism for an acid-catalyzed esterification. Find at least 2 factors that can affect the rate of the reaction (these need to be factors that you can monitor in your laboratory setting with a limited amount of chemicals).

Items Needed:

Deionized water	1-Pentanol
Spatula	Acetic acid (0.1M, 0.2M, 0.5M 1.0M, 2.0M)
Hot/Stir plate	Methanoic acid (0.2M)
Test tubes, 10 cm (long) x 1.5 cm (diameter) or smaller	Isobutyric acid (0.2M)
Test Tube rack	n-butyric acid (0.2M)
Large beaker (250-500 mL)	Concentrated H ₂ SO ₄
Acetone for washing	10mL beakers
Ethanol	Small Teflon ® stir bar
1-propanol	Watch with second hand or stopwatch
2-Propanol	Labels
Evaporation Dish	Fan/Stand/Clamp
	Thermometer

Warning: The sulfuric acid is corrosive and may cause burns. The organic acids are irritants with prolonged exposure and may be corrosive in *concentrated* solutions. Alcohols and acetone may cause skin irritations and are flammable reagents that should be kept away from ignitable sources. Consult instructor about chemical spills and burns. Instructor will demonstrate the best way to smell compounds (wafting). Direct inhalation of any compound may cause irritation.

Procedure:

Part A. Preparation of Various Esters: (Time Limit: 15 minutes)

You will be working in groups of 2-3 students. However, *each* student will be responsible for synthesizing a specific ester assigned by your instructor. Heat ~200 mL of water in a large beaker (~75-85°C). Locate the reagents you will need to make your assigned ester. Your instructor will not specifically tell you which compounds to use, as *you* will need to determine this from your pre-lab mechanism. Multiple reactions should be set-up at the same time (each student of the group is required to perform his/her own synthesis). Label your test tube. Add 20 drops of the required carboxylic acid (0.2M) to a test tube followed by 5 drops of concentrated H₂SO₄ (carefully). Place the test tube in the hot water then add 10 drops of the required alcohol.

Allow the reaction to sit in the hot water bath for about 10 minutes, occasionally swirling with a glass rod. Make a table in your notebook like Table 1 and note any observations. After 10

minutes, add 15 drops of water to the test tube (rinsing the sides of the test tube as you do this) and allow cooling in a cold water bath. Swirl the test tube, then waft and note the aroma being as descriptive as possible. You will then annotate the aromas of the different esters made in your group. You must work efficiently and in a timely manner.

Part B. Investigation of the effect of various reagents on the rate: (Time Limit: 50 minutes)

Assemble the set-up as shown in Figure 3.4 positioning the fan behind the hot plate but directly above the beaker. Add water to the evaporation dish to ~1/2 full and heat to about 75°C. Make a table similar to Table 1 in your notebook. You will perform the experiments based on this table. Each group of students will be assigned one carboxylic acid to perform kinetics studies with 4 alcohols with at least 2 trials each. To a 10 mL beaker, add 28 drops of your 0.2M carboxylic acid and 5 drops of concentrated H₂SO₄. Place a small Teflon® stir bar in the beaker, placing the beaker in the water bath and allow stirring. To this mixture, add 7 drops of the alcohol quickly. Start timing and turn on the fan. Position yourself at the edge of the lab bench, allowing your nose to be about 12 inches away from the beaker in the direction of the fan's airflow.

The first aroma you may notice is the alcohol, which may last for 1-2 seconds. Do not stop timing at this point. Record the time you observe the aroma of the ester (it must be longer than 3 seconds). You will run at least 2 trials for each alcohol. Repeat your trials a third time if the first two are not within 2 seconds of each other. In total, you will be using one carboxylic acid with 4 alcohols (minimum 8 runs). Turn the fan off in between trials to keep the bath temperature constant. Ensure that your water bath is at the desired temperature after each trial before continuing. Replenish the water bath as necessary.

Part C. Varying the amount of alcohol, acid concentration and amount of catalyst in the reaction: (Time Limit: 30 minutes)

Your instructor will assign each group of students one of these variations and you will be required to obtain the data from the other groups at the end of the experiment. You will run at least 2 trials repeating your trial a third time if the first two are not within 2 seconds of each other. You will perform Part C in the same way as part B, following the variations seen in Tables 3-5. Your standard conditions for Part C are 28 drops of 0.2 M acetic acid, 7 drops of ethanol and 5 drops of concentrated sulfuric acid. Various conditions of your experiment will change according to the tables. Table 2 shows how you will vary the amount of alcohol added, while keeping the other conditions constant. In Table 4 you will vary the concentration of the acetic acid and in Table 5 the amount of the sulfuric acid will be altered.

Table 1. Observations and aroma of esters.
Observed Aromas

<chem>CCCCO</chem>	<chem>CC(C)O</chem>	<chem>CCCO</chem>	<chem>CCO</chem>	← Alcohols ↓ Acids
				<chem>CC(=O)O</chem>
				<chem>CC(=O)O</chem>
				<chem>CCCC(=O)O</chem>
				<chem>CC(C)C(=O)O</chem>

Table 2. Rates of various reagents.
Time, seconds

<chem>CCCCO</chem>	<chem>CC(C)O</chem>	<chem>CCCO</chem>	<chem>CCO</chem>	← Alcohols ↓ Acids
				<chem>CC(=O)O</chem>
				<chem>CC(=O)O</chem>
				<chem>CCCC(=O)O</chem>
				<chem>CC(C)C(=O)O</chem>

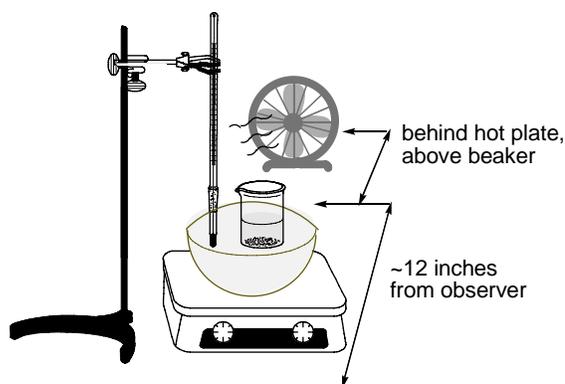


Figure 1. Esterification experimental set-up.

Table 3. Variation on the amount of alcohol.

$$\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{COOCH}_2\text{CH}_3$$

Drops of Alcohol	Time, sec
1	
2	
5	
7	
10	

Use 0.2 M Acetic Acid (28 drops); H₂SO₄ (5 drops)

Part D: Clean up:

Once you conclude your assignment for Part C, you must collect data from the other groups to complete Tables 1-5. Turn off your hot plate and allow cooling. Discard all organic waste in the corresponding waste container. Rinse your test tubes with acetone and discard the acetone in the organic waste bottle. Rinse your glassware thoroughly and allow to dry. Clean your lab bench, ensuring that you have left no chemicals on the bench. Put away any glassware or equipment used.

Table 4. Variation of Acetic Acid concentration

Concentration, M	Time, sec
0.1	
0.2	
0.5	
1.0	
2.0	

Use alcohol (7 drops), H₂SO₄ (5 drops)

Table 5. Variation of amount of catalyst

Amount of H ₂ SO ₄	Time, sec
1 drop	
2 drops	
5 drops	
10 drops	
20 drops	

Use alcohol, 0.2 M Acetic Acid (7 drops each)

Questions

- Using the data collected in Table 2, explain the rate of the reactions in terms of the factors that affect it.
- Using the results of Table 3, determine how the amount of alcohol affects the rate of the reaction.
- Based on your data in Table 4, how does the concentration of your carboxylic acid affect the reaction rate? Provide an explanation.
- With respect to Table 5, what conclusions can be drawn about the rate of reaction with respect to the sulfuric acid catalyst? Comment on how the catalysts affect the energetics of the reaction.
- Based on your observations, what would you expect the rate of formation of to be? Explain.
- Based on your observations, what were the trends in aroma of the esters you made?
- Predict what you would expect to happen to the rate of the reaction at various temperatures (high to low), knowing that this reaction is endothermic.
- What are the potential sources of error associated with this experiment?
- Extra Credit:* What possible competing reaction could be occurring and what compounds may be more prone to this side reaction? What factor would you expect to contribute to this reaction? You may use your textbook.

Esterification Instructor's Notes

Purpose: Fischer esterification is a type of esterification reaction that uses a carboxylic acid and an alcohol in the presence of an acid catalyst. Generally, primary and secondary alcohols and most carboxylic acids are suitable for this reaction (1). This reaction is typically done without the use of a solvent, but uses excess of one of the reagents, such as the alcohol (2,3). Students will identify characteristic aromas associated with esters and explore potential trends associated with various carboxylic acids or alcohols. Chemical kinetics involves the investigation of how various experimental factors affect the rate of a reaction, which gives information about the mechanism of the reaction (4).

Students will explore in a non-traditional way the factors that affect the rate of an acid catalyzed Fischer esterification such as structural effects, amount of alcohol, carboxylic acid concentration, and amount of catalyst. Students monitor the time taken for them to observe the emergence of the ester aromas, which is then used to infer the effects of the different factors on the rate of the reaction. Other factors that can be explored are temperature, type of catalyst, competing reactions, amount of carboxylic acid used and the properties of the esters that may affect their rate of diffusion. Students should be directed to use observations and data collected to answer related questions, which can lead them to an extension of the ideas presented to them. Students will also be asked to answer a question on which they have not performed experiments but have been given enough information to respond. The experiment is designed as an inquiry-based, therefore, only crucial information is given to the students.

Reagents used (CAS numbers):

Acetic acid - 64-19-7	Isobutyric acid - 79-31-2	1-Propanol - 71-23-8
Ethanol - 64-17-5	n-butyric acid - 107-92-6	1-Pentanol - 71-41-0
Methanoic acid - 64-18-6	2-Propanol - 67-63-0	Sulfuric acid - 7664-93-9

Preparation of reagents: All reagents are placed in small dropper bottles.

The desired amount of concentrated carboxylic acid according to Table C.1 is placed in a 1000mL volumetric flask containing ~ 500mL deionized water. The flask is filled to the 1000mL mark with the remaining deionized water and capped. The flask is shaken to ensure complete mixing.

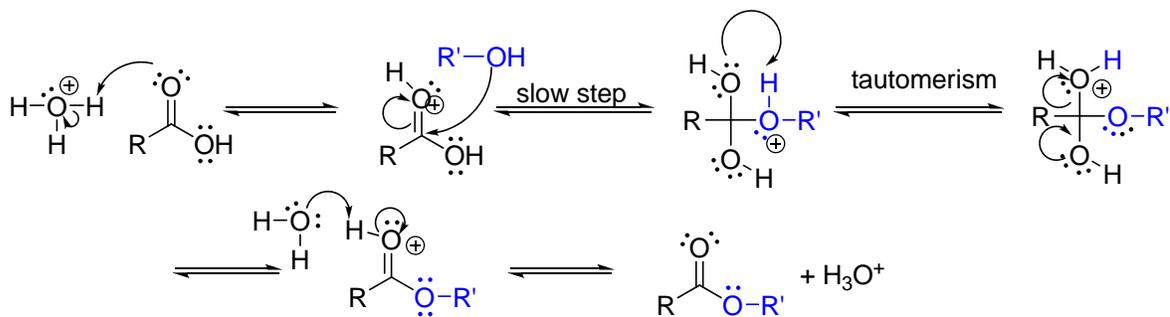
Table C.1. Amount of carboxylic acid needed to make solutions with various concentrations.

Concentration of Acid Needed	Amount of Concentrated Acid
~0.1 M Acetic acid	6.0mL
~0.2 M Acetic acid	11.0mL
~0.5 M Acetic acid	29.0mL
~1.0 M Acetic acid	57.0mL
~2.0 M Acetic acid	114.0mL
~0.2M Methanoic acid	7.60mL
~0.2M Isobutyric acid	19.0mL
~0.2M n-butyric acid	18.4mL

Hazards:

Sulfuric acid is corrosive and may cause burns. The organic acids (acetic, formic, isobutyric and n-butyric acid) are irritants with prolonged exposure and may be corrosive in concentrated solutions. The concentrated organic acids have strong odors. It is advised that these be prepared in the hood,

however the carboxylic acids are used in diluted concentrations by the students to avoid hazards. Alcohols (ethanol, 2-propanol, 1-propanol and 1-pentanol) are flammable reagents and should be kept away from ignitable sources. Alcohols are irritants with prolonged exposure and in high concentrations. General laboratory precautions need to be taken when preparing the chemicals, as well as when handling chemicals in the laboratory. The potential harmful effects of the alcohols, carboxylic acids and synthesized esters used in the laboratory have been minimized as they are used in minute quantities or diluted. Students do not directly observe any aroma, but must use a fan or waft the chemicals. Students should wear standard laboratory gear such as goggles, closed-toed shoes, and clothing that covers the torso and legs. The procedure for wafting should be demonstrated. Students should waft the chemicals as direct inhalation of any chemical may cause irritations.

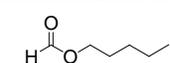
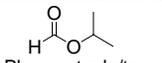
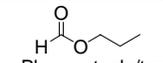
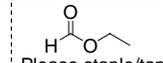
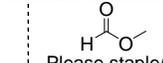
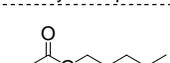
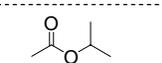
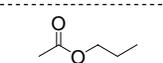
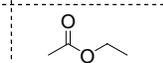
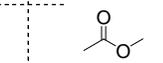
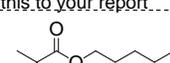
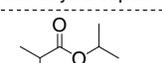
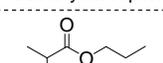
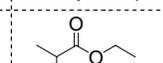
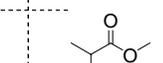
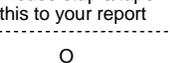
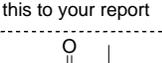
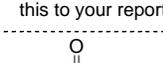
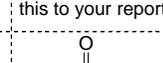
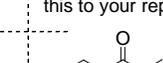


Scheme C.1. Fisher Esterification Mechanism

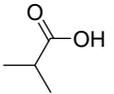
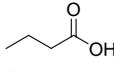
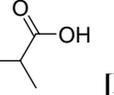
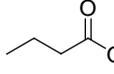
Suggestions and Notes

Experiment:

- Demonstrate to students how to smell the chemicals by wafting.
- *Aromas:* Allow the students to discuss their ideas in Part A. You may give a list of descriptive words for the students to refer to. Some students may have difficulty classifying their aroma.
- Students will work as a group for Parts B and C and may assign members specific tasks to work faster. If a student has difficulty smelling (in Part A), someone else should determine the rates in Parts B and C.
- Have specific tasks divided up before the experiment and handed out to each student and each group. Each student will have to prepare one ester for Table 1. They will share the laboratory equipment with their group members, but will work individually to prepare the ester. Each group must perform kinetics tests (together) for one carboxylic acid in Table 2 (4 alcohols) and each group will be assigned either Table 3, Table 4 or Table 5 of the student procedure. The students will share their data in order to complete all tables and be able to answer questions. A template on how the parts may be divided is shown in Figure C.1 below.

Assigned to group 1 ⇒	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report
Assigned to group 2 ⇒	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report
Assigned to group 3 ⇒	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report
Assigned to group 4 ⇒	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report	 Please staple/tape this to your report

Part A: Esters assigned to students

 [B] Table 3 [C] (Assigned to group 1)	 [B] Table 4 [C] (Assigned to group 2)	 [B] Table 5 [C] (Assigned to group 3)	 [B] Table 3 [C] (Assigned to group 4)
 [B] Table 4 [C] (Assigned to group 5)	 [B] Table 5 [C] (Assigned to group 6)	 [B] Table 3 [C] (Assigned to group 7)	 [B] Table 4 [C] (Assigned to group 8)

Part B and C

Figure C.1. Template for which individual students and student groups are divided for each part of the procedure.

Note: For Part A, each student in the group should be assigned an ester that requires the same acid, however they should not be told this. The students are required to decide what carboxylic acids and alcohols are required to produce their assigned esters. In Part B, students should be assigned the same carboxylic acids that they used in Part A to prepare their esters in order to reduce the amount of aromas that they will have to smell and be exposed to. This may reduce contaminations and desensitization of the sense of smell.

Optional:

- A variation to this experiment would be to plot graphs in order to determine the rate of the reaction. One reaction (carboxylic acid and alcohol) may be chosen for the students to explore, as this would require a significant time portion of the experiment.
- More advanced students may explore the effects of vapor pressure on the time it takes for the smell to emerge, as well as looking at the boiling points of the compounds used. Students may find a correlation between vapor pressure and the time the reaction takes to be detected.

Write-up/Post-Lab:

- *Data collection:* Groups may write their results on the board or may be paired with other groups to collect the remaining data. The data may be collected by the instructor and the best data presented on the board.

- Various alcohols may be used.

Notes on procedure:

- The most likely sources of error are students not correctly placing the set-up ~12 inches away and students indicating the smell of the alcohols instead of the esters.

- As indicated in the students' instructions, students may initially observe the aroma of the alcohol, therefore, they must wait about 1-2 seconds before observing ester aromas.

- The students must sit in the direction of airflow from the fan in order to accurately detect the aroma.

- It is very important that the temperature of the water bath is kept relatively constant during the reaction.

- You may put tape on the bench to indicate the appropriate distance for the set-up.

Equipment and measures for prevention of overwhelming aromas:

- Various hand-held, portable or desk fans may be used. They must, however, be small enough to point primarily over the beaker as well as blow the air relatively weakly i.e. have a low setting.

- Allow the students to take breaks between each part of the experiment.

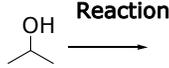
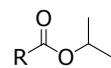
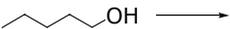
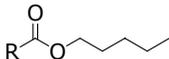
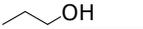
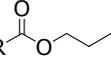
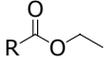
- Offer smelling coffee crystals between trials.

- If the lab is equipped with hoods in the benches, students should position the set-up inside the hood (but the hoods should be off or airflow must be at a minimum).

- Unnecessary chemicals should remain closed and in a fume hood until needed for a reaction.

- Dropper bottles help to cut down on aromas in the laboratory.

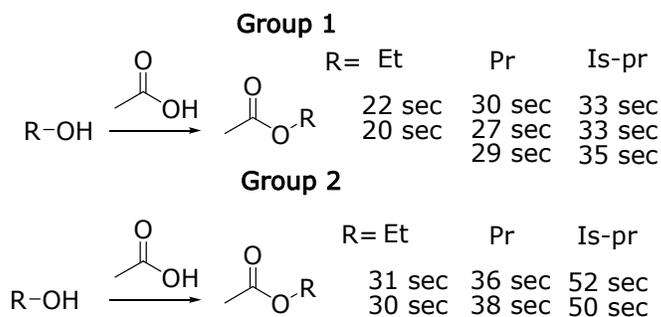
Table C.2. Sample data for students' results for Table 2.

Reaction	R from carboxylic acid =	Time Ranges (data from four groups)			
		H	Me	Pr	Is-pr
		12±1sec n=2	20sec n=2	24±1sec n=2	26±1sec n=2
		8±1sec n=3	18±2sec n=3	23±1sec n=2	16±1sec n=2
		10±1sec n=2	15±1sec n=2	22±1sec n=2	24sec n=2
		5±1sec n=3	9±1sec n=3	15±1sec n=3	19±1sec n=2

n - trials

Since each group is assigned a carboxylic acid in Part B, they should be able to observe the trend that as the chain length and the steric bulk of the alcohol increases, the time taken for the aroma to emerge increases as well. An example of the data collected from four groups in the various sections of the organic laboratories is shown in Table C.2. Based on the results of the students, it did not matter the magnitude of their numbers, the students were able to observe a general trend in the data. Table C.3 shows how varied the data from various groups of students can be. Group 1 obtained values that were closer together, while group 2 had a wider spread of values.

Table C.3. Example of the variability of results of two groups of students.



Advanced Experimentation:

The student's data may vary among the groups, but general trends are observed. Each student group observe the trends, but the time will vary based on how well they perform the experiment and how easily they detect the esters. Other factors that affect the time for the emergence of the esters were not explored with these beginning organic students because of their skill level and information covered in lecture. Some of the factors that affect the time taken to observe the aromas such as vapor pressure (volatility), and boiling point may be explored in more advanced laboratories. Students may note that compounds with increased vapor pressures or increased volatility may affect the time taken for the emergence of the aroma, which may explain significant time differences between certain esters. Table 3.5 shows that many of the esters produced in this experiment have similar odor threshold values (lowest concentration of a compound perceivable by the majority of the population,) and estimated values may vary slightly depending on methods use by the experimenter (5-7). In this experiment, the concentration of the esters used exceeds the literature values making them relatively easy to perceive. These esters have a relatively high reaction conversion of up to ~85-90% when one of the reagents is used in excess (3,6).

The students' values will have a range depending on how accurate they are and how carefully they followed the directions. The values the students obtain may also vary slightly from each group even if they perform the experiment correctly as some students' sense of smell may be slightly sharper than others.

Table C.4. Sample of volume equivalents for reagents drops used in Part B.

Reagent added	Measured equivalent volume	Moles
7 drops ethanol	<0.1mL	<1.7mmol
28 drops 0.2M acetic acid	2.0mL	0.4mmol

An excess of alcohol is used to promote high conversion to the ester (Table C.4), and allow for the students to smell the ester relatively easily (3,6).

Additional data and Answers

Instructors and Sample Student Responses Questions

1. Using the data collected in Table 2, explain the rate of the reactions in terms of the factors that affect it.

Instructor answer: *Due to the sterics of a primary or secondary alcohol, the rate of the reaction would be slower. The same is also true for the acids. Because of the steric bulk associated with the additional methyl groups or longer chains on the carboxylic acids compared with the acetic acid, the reaction is slower or does not occur.*

Sample student answers:

“The larger the desired ester, the longer it takes to create them. Bulky molecules have more trouble moving around each other.”

“Reactions took longer and longer time with increasing chain length and branching of both alcohols and carboxylic acid. Shorter unbranched chains have greater reactivity due to more room.”

2. Using the results of Table 3, determine how the amount of alcohol affects the rate of the reaction.

Instructor answer: *Increasing the amount of alcohol, would increase the rate of the reaction as the excess alcohol drives the progression of the reaction with the consumption of the carboxylic acid. Since the alcohol takes part in the rate determining step, increasing the amount of alcohol (its concentration) affects how fast the reaction takes place as the rate of reaction depends on the slowest step.*

Sample student answers:

“An increased amount of reactants caused the rate to go up.”

“As the amount of alcohol increase, the rate of reaction increases (more reactant → more product).”

“With increasing amount of alcohol in the solution, time of the reaction decreased. More alcohol reactant pushed the reaction to go faster.”

3. Based on your data in Table 4, how does the concentration of your carboxylic acid affect the reaction rate? Provide an explanation.

Instructor answer: *Increasing the concentration in effect increases the overall amount of carboxylic acid present in the solution without changing the overall volume of the reaction. The amount of carboxylic acid present affects how fast the reaction occurs.*

Sample student answers:

“The rate increases due to the higher concentration which provides more reactants.”

“Generally, the higher the concentration, the more reactant, much as above, so the reaction rate increases decreasing time.”

4. With respect to Table 5, what conclusions can be drawn about the rate of reaction with respect to the sulfuric acid catalyst? Comment on how the catalysts affect the energetics of the reaction.

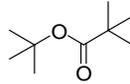
Instructor answer: *Increasing the amount of the catalyst will increase the rate of the reaction. However, at certain concentration, the catalyst will have no further effect on the rate of the reaction. The catalyst lowers the activation energy of the reaction by protonating the carboxylic acid. Once all the carboxylic acid is protonated the catalyst causes no effect to the reaction rate.*

Sample student answers:

“The reactions increases with amount of sulfuric acid catalyst that is added. At high concentrations, the reaction will continue to increase until a point where they will remain the same. The catalysts decreases initial energy needed for the reaction to occur.”

“The higher the amount of H₂SO₄, the faster the reactions takes place. At high concentrations, the reaction takes place faster. Catalysts lower activation energy and are present at both the beginning and end of the reaction.”

“The reactions increases with amount of sulfuric acid catalyst that is added. At high concentrations, the reaction will continue to increase until a point where they will remain the same. The catalysts decreases initial energy needed for the reaction to occur.”

5. Based on your observations, what would you expect the rate of formation of  to be? Explain.

Instructor answer: *The rate should be extremely slow and possibly might not occur readily. This would be due to the steric effects of the t-butyl groups of the alcohol and the carboxylic acid. The steric bulk associated with three methyl groups inhibits or prevents the interactions of the groups to form the ester.*

Sample student answers:

“Relatively slow due to large bulky substituents”

“I would expect it to be slow because of the more complex carboxylic acid group and alcohol group.”

“Having multiple substituted carbon chains on each end of the compound will merit slowly[ed] reaction time.”

6. Based on your observations, what were the trends in aroma of the esters you made?

Instructor answer: *There were no definite trends; the answer is dependent on the student. However, the n-butyl esters aromas resemble apple or pineapple odors. The other esters have sweet or fruity aromas and depending on the table formed at the end of Part A a trend may be seen for other esters.*

Sample student answers:

“All of the 1-propanol created sweet fruity smells as well as the ethanol. The others seemed random.”

“Most trends were toward fruity or fruit like aromas, especially with ethanol.”

“Based on table 1, it seems more complex ester have nicer smells (except for a few exceptions).”

“The aromas tended to depend more on the alcohols used than on the carboxylic acids.”

“Isobutyric acid yields the most fruity smells.”

7. Predict what you would expect to happen to the rate of the reaction at various temperatures (high to low), knowing that this reaction is endothermic.

Instructor answer: *At lower temperatures the reaction would not occur readily. At higher temperatures the reaction would be faster. However, temperature is an issue with volatility of reactants and products.*

Sample student answers:

“It would increase to a certain extent. After a while it does not matter because there is a cut off point for the reaction. Increased temp does increase the rate because the compound interacts faster. It evaporates.”

“Endothermic reactions take in heat and use it. If the temperature cools off, the reaction may not happen as efficiently. If temps. got too hot, the solution may evaporate.”

8. What are the potential sources of error associated with this experiment?

Instructor answer: *Incorrectly measuring the reagents used. Not having the fan above the beaker. Not allowing the water bath to reach the stated temperature between trials. Differences in aroma detection times between groups.*

Sample student answers:

“Sources of error are not smelling things we do so many smell present around us, possibly adding too much or not enough of certain concentration, temperature varying and not exactly being at 78C.”

“Insensitive noses, bad timing and improper wafting techniques can all contribute to errors in this experiment.”

9. *Extra Credit:* What possible competing reaction could be occurring and what compounds may be more prone to this side reaction? What factor would you expect to contribute to this reaction? You may use your textbook.

Instructor answer: *Bulky alcohols can undergo an elimination reaction, which would produce an alkene. More heat added to the reaction would induce an elimination reaction. The central carbon is a stable carbocation due to the electron releasing nature of the methyl groups. Solvolysis may also occur in the reaction where S_N1 is favored at lower temperatures and E1 at higher temperatures.*

Sample student answers:

“The presence of strong bases such as OH⁻ may create alkenes through an elimination reaction.”

“Competing reactions could occur due to the equation’s reversibility at some point sufficient water as leaving group might drive the reaction leftward favoring carboxylic acid. Also the water added in part A might do this. (We mistaking used tap water and its chlorine might compete too). The compounds more prone to side reactions would be the larger branched ester with more room on them to react with the water (more H atoms on them).”

Some student feedback:

“I thought that the experiment was interesting because we got to use our noses to sense when reactions take place. We do not normally get to do this, we usually use instrumentation.”

“I thought the experiment was good because being the measuring device was interesting. To know when it was happening without the fancy machines was nice. It also gave good insight into the different contributors to reaction speed, with noticeable changes which we measured.”

“Experiment was interesting, ‘real chemistry’. That each aspect of a reaction can influence its rate is instructive, particularly when working toward a specific quantitative result.”

Table C.5. Number of students responses by correctness as percentages for esterification pre and post lab questions.

Questions	Points	Concepts	C&C	C	N
Pre-lab					
Chemicals	1	Alcohols, carboxylic acids and esters.	80%	0%	20%
Mechanism	5	Draw acid catalyzed mechanism	72%	3%	24%
Factors	2	State 2 factors that affect rate.	59%	6%	34%
Post lab					
Table 2 - analysis	8	Structure-Activity	45%	43%	11%
Table 3 - analysis	8	Concentration of alcohol	14%	77%	8%
Table 4 - analysis	8	Concentration of carboxylic acid	29%	59%	11%
Table 5 - analysis	8	Catalyst	32%	55%	11%
Knowledge utilization	5	Rate of <i>tert</i> -butyl pivalate	66%	21%	14%
Analysis	2	Aroma trends	62%	17%	18%
Knowledge utilization	5	Temperature effects	53%	24%	23%
Metacognition	6	Recognition of experimental errors	62%	16%	20%
Knowledge utilization	6	Possible side reactions	21%	16%	61%
Metacognition	2	Suggest improvements	16%	13%	69%

Complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N). C&C responses provided above.

References:

- Solomons, T.W. G.; Fryhle, C. B. *Organic Chemistry*, 7th edition, John Wiley and Sons, New York, **2000**.
- Ishihara, K.; Nakayama, M.; Ohara, S.; Yamamoto, H. *Tetrahedron*, **2002**, *58*, 8179–8188.
- Vollhardt, K.P.C.; Schore, N.E. *Organic Chemistry*, 2nd edition, W.H. Freeman and Company, New York, **1994**, page 739.
- O'Lenick, Jr.; Anthony, J.; Parkinson, J. K. *J. Soc. Cosmet. Chem.* **1994**, *45*, 247-256.
- Takeoka, G.; Buttery, R.G.; Ling, L. *Food Sci. and Tech.* **1996**, *52*, 677-680; Takeoka, G.; Buttery, R.G.; Turnbaugh, J.G.; Benson, M. *Food Sci. and Tech.* **1995**, *28*, 153-156; Salo, P.; Nykänen, L.; Suomalainen, H. *J. Food Sci.* **1972**, *37*, 394-398; Measurement of Odor Threshold by Triangle Odor Bag Method. http://www.env.go.jp/en/air/odor/measure/02_3_2.pdf (Last accessed December 7th, 2007); Sigma-Aldrich MSDS online. www.sigmaaldrich.com (Last accessed 15th January, 2008).
- Liu, Y.; Lotero, E.; Goodwin, J. *J. Catal.*, **2006**, *243*, 221-228.
- Buttery, R.G.; Ling, L.; Guadagni, D.G. *J. Agr. Food Chem.* **1969**, *17*, 385-389.; Takeoka, G. R.; Flath, R.A.; Mon, T. R.; Teranishi, R.; Guentert, M. *J. Agric. Food Chem.* **1990**, *38*, 471-477. Sigma-Aldrich MSDS online. www.sigmaaldrich.com (Last accessed 15th January, 2008).

Appendix D . Le Chatelier's and equilibrium study

Dynamic Equilibrium and an introduction to the Le Chatelier's Principle Activity

Instructor's Notes:

The pedagogical objectives of this activity are based primarily on the taxonomy of educational objectives of Marzano and Kendall (*I*). Marzano and Kendall presented a tool for classifying learning objectives, creating assignments, and teaching critical skills utilizing the concept knowledge construction consists of three systems of thinking (self, metacognitive, and cognitive).

Objectives:

- Students will observe constant motion of the reactants and reagents and observe dynamic equilibrium as both forward and reverse reaction occur at the same time (knowledge utilization and analysis).
- Students will investigate concentration changes in a reaction as it comes to equilibrium at a constant temperature and produce graphs of concentration vs. reaction progress (comprehension).
- Students will observe the effects of perturbation and construct graphs reflecting their data (knowledge utilization and comprehension).
- Students will define Le Chatelier's principle from the data produced (analysis).
- Students will solve problems with equations involving K_{eq} , k_f , and k_r using their data and relate features of equilibrium with the equations (retrieval).

Type of activity: Inquiry/discovery for a class of ~100 students in 4 groups.

Time needed: 20 minutes

Overview:

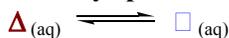
This activity is a demonstration of equilibrium requiring the *active* participation of students as students represent atoms and molecules in a reaction taking place in a hypothetical reaction flask (2). Each group consists of 20-25, where students are chosen to act as molecules, one student records data and remaining students act as "extent-keepers". Different students are chosen for each part of the activity to allow students to play different roles. The "molecules" are in constant motion in the "flask" and perform transformations between reactant and product which are constantly taking place.

The "extent-keepers" (remaining students) ensure that the correct number of transformation have occurred when the instructor makes a sound such as a chime, music or buzzer depicting the progression of the reaction. The signal given marks a pause in reaction progress for which "extent-keepers" ensure the correct transformations occurred. The "record-keepers" documents the changes in the reaction progression on the board or their sheet by documenting the number of molecules present at each sound signal. Students are given the conditions of the reaction and the amount of conversion for the forward and reverse transformations occurring at each chime. Using the data obtained calculations of concentration and K_{eq} can then be done. Each group is assigned slightly different conditions and number of molecules.

Finally, the reaction experiences changes in temperature and addition or removal of a reagent to observe the effects of perturbation. The roles for each student are changed to allow all students to have experience the reaction from different viewpoints. Students are given different conditions for a temperature change and explore why the forward and reverse reactions proceed differently. Additional the student molecules are used to show the changes that occur with adding a

reagent, which leads them into the discussion of Le Chatelier's principle (3). Students draw graphs, collect data from all the groups and discuss among their groups the idea of dynamic equilibrium.

Activity specifics:



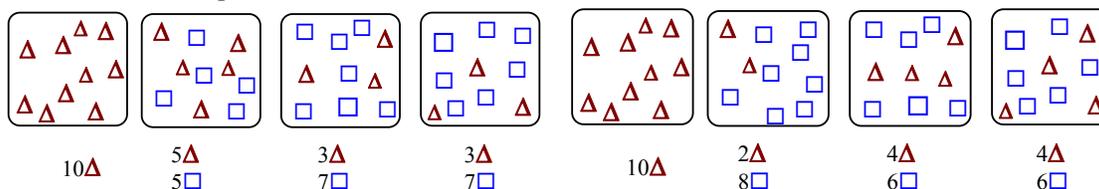
Part A: Four sections of the room are marked off as squares or circles to depict a 0.10L reaction flask. The student molecules are placed in the 'flask', holding up their Δ signs (Δ molecules are the starting materials). The students slowly but continuously move around as the reaction starts flipping their signs occasionally as they move. When given the signal, some students have reacted to form \square molecules. Each time the signal is given and the transformation occurs, the "extent-keepers" help to ensure the correct number of students make the change. The recorder reports the amount of each molecule at each interval, which is used for the calculations.

The conditions given to the students that promote the forward reaction to a greater extent are at room temperature (25°C) and pressure. Groups 1 and 2 start with 10 Δ , while groups 3 and 4 with 12 Δ .

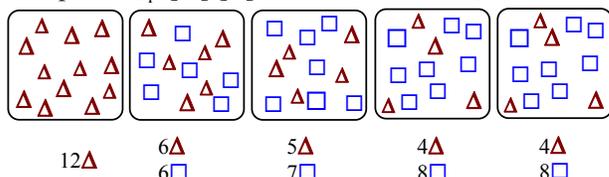
The conversion value for groups 1 and 3 are $\frac{1}{2} \Delta \rightarrow \square$; where $\frac{1}{2}$ of the Δ molecules reacting to become \square at each interval, while only $\frac{1}{4}$ of the \square can become the reactants. Group 2 use $\frac{3}{4} \Delta \rightarrow \square$ and group 4 $\frac{1}{2} \Delta \rightarrow \square$.

Results:

Once reaction has reached dynamic equilibrium (stabilized concentrations), students use that data to calculate equilibrium constant.



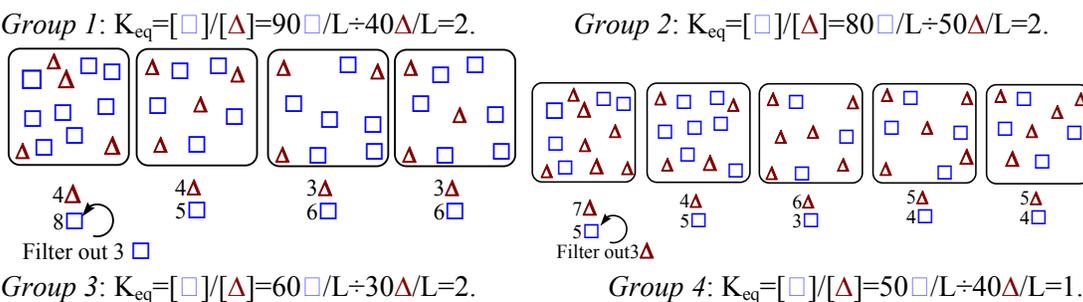
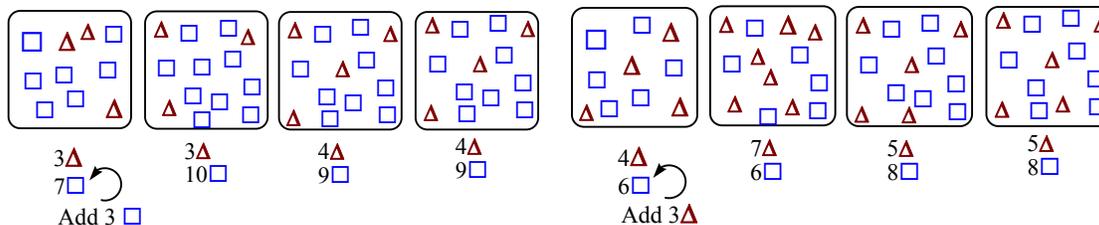
Group 1: $K_{eq} = \frac{[\square]}{[\Delta]} = \frac{70 \square / L}{30 \Delta / L} = \frac{k_f}{k_r} = 0.5 / 0.25 = 2$
 Group 2: $K_{eq} = \frac{[\square]}{[\Delta]} = \frac{60 \square / L}{40 \Delta / L} = \frac{k_f}{k_r} = 0.75 / 0.5 = 2$



Group 3: $K_{eq} = \frac{[\square]}{[\Delta]} = \frac{80 \square / L}{40 \Delta / L} = \frac{k_f}{k_r} = 0.5 / 0.25 = 2$
 Group 4: $K_{eq} = \frac{[\square]}{[\Delta]} = \frac{70 \square / L}{50 \Delta / L} = \frac{k_f}{k_r} = 0.75 / 0.5 = 1$

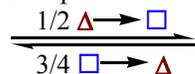
Part B: This system is then perturbed by adding or filtering out Δ or \square to the reaction and repeating the same conditions to re-establish equilibrium, and based on their calculations observe K_{eq} remains the constant at equilibrium.

Results:

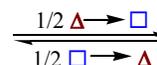


Part C: The temperature is changed for each group, but the pressure remains constant. Students are asked what happens to the motion of the molecules in the flask with increased or decrease temperature for endothermic or exothermic reactions. Each group is given new conversion values, allowing them to observe the effects of temperature. They are again asked to show this reaction, mimicking changes based on the exchange rate, and decide the resulting K_{eq} .

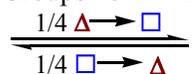
Group 1 - Reverse reaction endothermic and temperature increased to 50°C at 1atm:



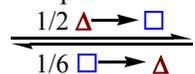
Group 2 - Forward reaction exothermic and temperature decreased to 10°C at 1atm:



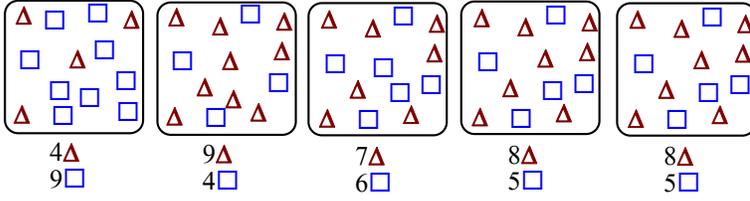
Group 3 - Forward reaction exothermic and temperature increased to 50°C at 1atm:



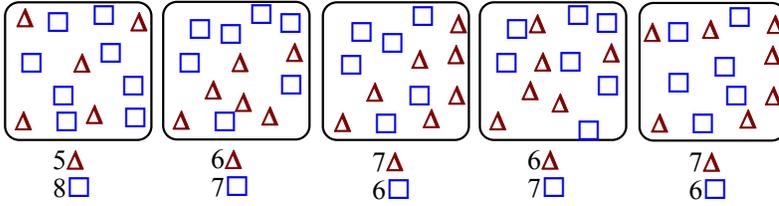
Group 4 - Reverse reaction endothermic and temperature decreased to 10°C at 1atm:



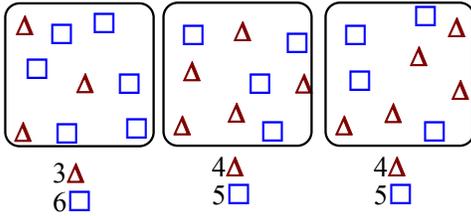
Results:



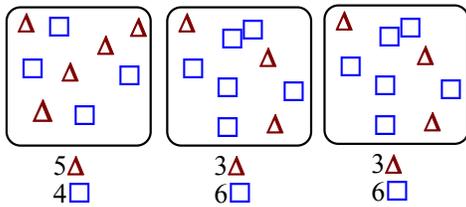
Group 1: $K_{eq} = [\square]/[\Delta] = 50 \square/L \div 80 \Delta/L = k_f/k_r = 0.5/0.75 = 1$.



Group 2: $K_{eq} = [\square]/[\Delta] = 60 \square/L \div 70 \Delta/L = k_f/k_r = 0.5/0.5 = 1$.



Group 3: $K_{eq} = [\square]/[\Delta] = 50 \square/L \div 40 \Delta/L = k_f/k_r = 0.25/0.25 = 1$



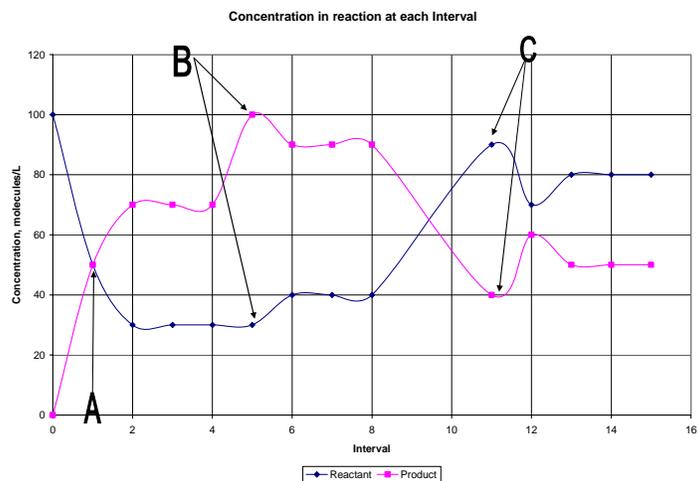
Group 4: $K_{eq} = [\square]/[\Delta] = 60 \square/L \div 30 \Delta/L = k_f/k_r = 0.5/0.25 = 2$.

Table 2. Complete data and calculations obtained from all parts of the activity for group 1.

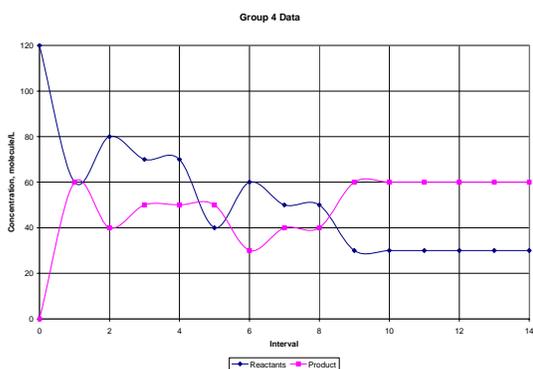
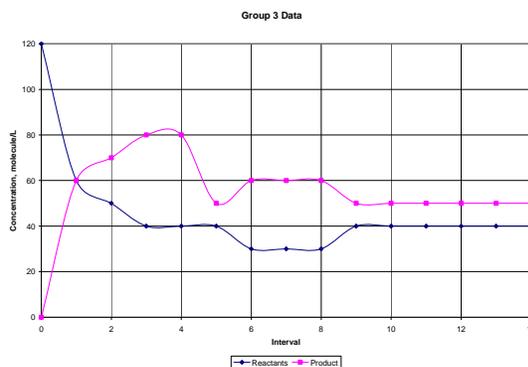
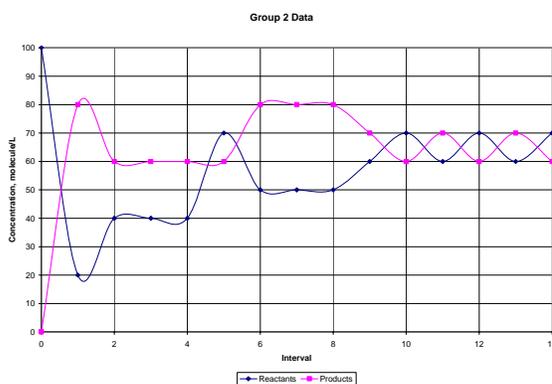
<i>Group 1:</i>	Interval	# of Δ	# of \square	$[\Delta]$, Δ/L	$[\square]$, \square/L
	0	10	0	100	-
Part A: Reaction starts	1	5	5	50	50
	2	3	7	30	70
	3	3	7	30	70
	4	3	7	30	70
Part B: Add 3 \square	5	3	10	30	100
	6	4	9	40	90
	7	4	9	40	90
	8	4	9	40	90
Part C: 50°C	9	9	4	90	40
	10	7	6	70	60
	11	8	5	80	50
	12	8	5	80	50
	13	8	5	80	50

Table 1. Complete data obtained from all parts of the activity for groups 2-4.

	Interval	<i>Group 2</i>		<i>Group 3</i>		<i>Group 4</i>				
		$[\Delta]$	$[\square]$	$[\Delta]$	$[\square]$	$[\Delta]$	$[\square]$			
	0	100	0	12	0	12	0			
Part A	1	20	80	60	60	60	60			
	2	40	60	50	70	80	40			
	3	40	60	40	80	70	50			
	4	40	60	40	80	70	50			
Part B	5	Add 3 Δ	70	60	Filter 3 \square	40	50	Filter 3 Δ	40	50
	6		50	80		30	60		60	60
	7		50	80		30	60		50	40
	8		50	80		30	60		50	40
Part C	9	10°C	60	70	50°C	40	50	10°C	30	60
	10		70	60		40	50		30	60
	11		60	70		40	50		30	60
	12		70	60		40	50		30	60
	13		60	70		40	50		30	60



Graph 1. Representative pre-lab activity concentration vs. interval/time graph.



Graphs 2-4. Data representing Groups 2-4 data for all parts of the activity.

The lines on these graphs are provided as a visual reference only.

Things Needed

- 1) Assigned students to act as molecules, and “record-keeper” to write on the board or on their sheet. Different students are used in each part of the activity.
- 2) "Extent-of-reaction-keepers" (remaining students) stand around the flask to help determine number of each molecule.
- 3) Δ - \square sign- a sheet of paper with each symbol on either side.
- 4) Paper/painter's tape (preferably brightly colored).
- 5) Chimes/music/sound signal.

Instructions for students

- Assign the students for each role in each part of the activity. Ask students to record data on the board or on the sheets.
- Explain the methods to determine K_{eq} . Assign and explain the use of conversion values.
- Explain K_{eq} and the above 2 methods that they use to obtain it. Briefly explain how to round: they only round up numbers that are a $\frac{1}{2}$ molecule or more, anything less gets round down.

Part A: Explain the activity briefly. Instruct “molecules” (all labeled as Δ) to move constantly and randomly at a moderate pace in the reaction flask to music or waiting for a signal, but occasionally changing their signs. Once the cue is given, the reaction is “paused” and they exhibit the conversions, where “extent-keepers” ensure the correct conversion has taken place by helping the molecules to have the correct number of conversions. The data is recorded before the music begins again or when given another signal. After 4 intervals, the students begin Part B.

Part B: Additional “molecules” are added to the current reaction and the students repeat as they did in Part A. Again this reaction is under the same pressure and temperature conditions, which should be emphasized. The students continue for 4 intervals.

Part C: Indicate that the temperature change at the same pressure, and consider how this affects the reaction. Refer them to questions 4-6.

Notes:

- If music is used, play a slightly faster music to hint to the students to move faster or play slower music for a decrease in temperature. Each music clip or time interval should be ~ 10 -15 seconds.
- Students are deliberately not given the conversion values ahead of time in order that they do not attempt to do the activity ahead of time. These values may be given to the students verbally or written on a sheet of paper.
- The terms “shift” and “rate” are not to be used in this activity, but rather the process explained using concentration and conversion of products and reactants. “Time” is also not used, but replaced with reaction progression so as not to lead the students to kinetic factors.
- Students should copy the data from the other groups in the second table and draw graphs, then answer the questions together.

Difference from other activities to prevent misconceptions:

- Constant motion and transformation of molecules, where the students are encouraged to constantly move in random motions while constantly changing their signs. This encourages the idea of dynamic equilibrium as well as that the molecules are constantly moving and reacting.
- Both forward and reverse reactions are done in one ‘flask’, with the elimination of the movement from side to side. This removed the idea of ‘sidedness’.
- Explore concentration changes and extent of reaction with relation to equilibrium constant leading into dynamic equilibrium discussion.

- Rather than talking about “shifts” in the reaction, students learn to access Le Chatelier’s principle in terms of concentration changes.
- This exercise involves the elimination of rate specific terminology and incorporation of simplified explanations in an inquiry format. Removal of the use of the terms and ‘rate’. These terms are replaced with changes in concentration and conversion of products and reactants. ‘Interval’ is used rather than a specific time to remove the concept of time dependence.

Modifications:

- If students with visual difficulties are in the class, you may use shapes, rather than color (if color blind). Very large signs may be used with students with low vision, or for students with low or no vision the shapes may be cut out producing very obvious tactile shapes. The student can actively participate by changing the shapes of the other students’ signs by the shape.
- Another equation that can be used is: $BR_{(aq)} \rightarrow B_{(aq)} + R_{(aq)}$, where B is a blue molecule and R is a red molecule. The students pair up for the $BR_{(aq)}$ molecules and remove from their partner the represent the products. Twice as many student molecules would be needed.
- This activity may be done in smaller groups as a non-active exercise using cards or coins, which can be flipped to represent reactants or products (3).
- Fewer students may be used also by eliminating any of the groups.
- The exercise can be combined with a more specific experiment or as a class room demonstration.
- Any “volume” for the reaction flask can be chosen.

References

1. Marzano, R.J., Kendall, J.S. *The New Taxonomy of Educational Objectives*, 2nd Ed. **2007**, Corwin Press, California.
2. Battino, R. *J. Chem. Edu.* **1975**, 52, 55. A dynamic lecture demonstration of dynamic equilibrium-the BG system.
3. Allen, D. A. 2005, The Development and Assessment of an Active Learning environment: $cAcL_2$, concept Advancement through chemistry Laboratory-Lecture. PhD thesis, North Carolina State University.; Wilson, A. H. *J. Chem. Edu.* **1998**, 75, 1176. Equilibrium: A Teaching/Learning Activity.; Chang, R., Thoman, *Chem. Educator*, **2001**, 6, 360-361.

Intervention Activity: As shown in the instructor's notes, each group has similar worksheets but with differing disturbances which include: addition of 1Δ and decrease in temperature (group 2), filtering out $3\Box$ and increase in temperature (group 3) and filtering out 2Δ and decreasing the temperature (group 4). Each group handout also has questions related to the specific disturbances. An example is shown.

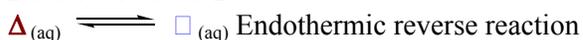
Le Chatelier's and equilibrium study Intervention Activity

Group 1: Student Activity Sheet: Dynamic Equilibrium and an introduction to the Le Chatelier's Principle Activity

Objective: Explore dynamic equilibrium and Le Chatelier's principle.

Procedure: In your group, some students are chosen to pretend to be "molecules" in a reaction flask while one student is a record-keeper. The remainder of your group aids the molecules during their reaction ("extent-of-reaction-keepers"). Your role in the group changes in each part of the activity. Further instructions are given by your instructor. Complete the Table 1 and draw a graph of concentration vs. interval to represent the data and answer the questions below. In Table 2, fill in the concentration changes of the other groups then draw the graphs.

All numbers are whole numbers, as you can't have fractions of molecules. You must only round up numbers that are a 1/2 or more, anything less gets round down. For example 1.5 is rounded to 2 and 2.3 is rounded to 2.



Method 1: $K_{eq} = [\Box]/[\Delta]$

Method 2: $K_{eq} = K_{eq} = k_f/k_r$ (forward conversion/reverse conversion)

Conversion factors- Part A and B: _____ Part C: _____

Reaction Conditions- Part A and B: 25°C and 1atm; Part C: 50°C and 1atm.

Volume of solution: 0.10L

Table 1	Interval	# of Δ , molecules	# of \Box , molecules	$[\Delta]$, Δ/L	$[\Box]$, \Box/L
	0	10Δ	$0\Box$	$100\Delta/L$	$0\Box/L$
Part A: Reaction begins	1				
	2				
	3				
	4				
Part B: Addition of $3\Box$	5				
	6				
	7				
Part C: 50°C	8				
	9				
	10				
	11				

	12				
	13				

Table 2		Group 2		Group 3		Group 4	
	Interval	[Δ]	[\square]	[Δ]	[\square]	[Δ]	[\square]
	0	100 Δ /L	0 \square /L	120 Δ /L	0 \square /L	120 Δ /L	0 \square /L
Part A	1						
	2						
	3						
	4						
Part B	5	Add 3 Δ		Filter 3 \square		Filter 3 Δ	
	6						
	7						
Part C	8						
	9	10°C		50°C		10°C	
	10						
	11						
	12						
	13						

Questions:

- Print/draw your graph (on another sheet), correctly labeling the axes and label the areas of the graph that correspond to each parts A-C. What do you notice about the progression graph? When was the reaction taking place at constant concentrations (unchanging)? What is the term for this phenomenon?

- What do you think would happen if you added more reactant rather than product?

Concentration products:	Concentration of reactants:
-------------------------	-----------------------------

- Calculate K_{eq} using methods 1 and 2 for each Part A-C (round values).

K_{eq}	Method 1	Method 2
Part A		
Part B		
Part C		

What do you notice about the values you obtain from each method and in Parts A-C?

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4. Draw what happens to the molecules when the temperature is increased? How does heat affect the *endothermic reverse* reaction (concentration of products and reactants) and affect K_{eq} ?

Diagram:	Effect: Reaction – K_{eq} -
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5. What if the reaction was exothermic and you increased the temperature? Decreased the temperature?

<i>Increased Temperature</i>	<i>Decreased Temperature</i>
Concentration products:	Concentration products:
Concentration of reactants:	Concentration of reactants:

6. Using your text book's definition of Le Chatelier's principle, write in your own words a *new* definition that includes the ideas you have explored in this activity.

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Equilibrium and Applications of Le Chatelier's Principle Pre-Laboratory Questions (Revised)

Name: _____
 T.A.: _____ Date: _____

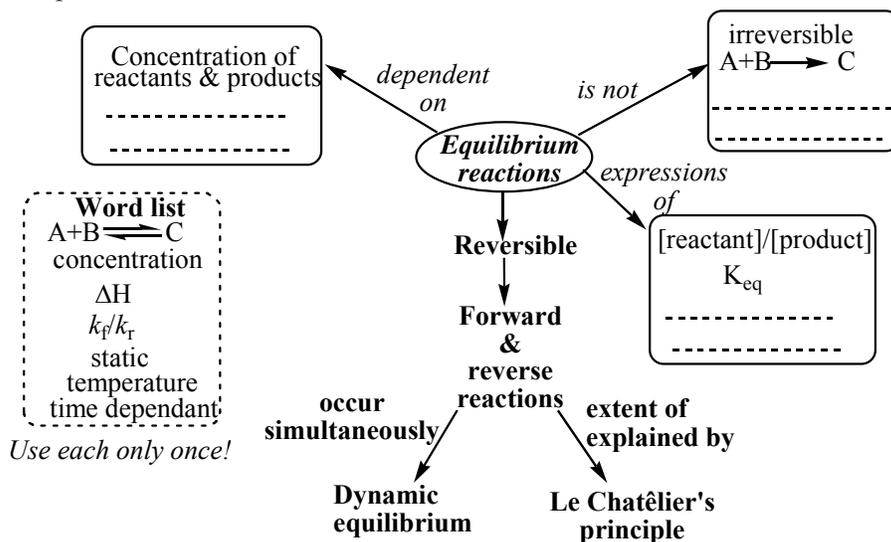
Equilibrium and Applications of Le Chatelier's Principle

Note: These pre-lab questions **must** be completed before the lab and turned to the instructor on the date announced. **Read the entire experiment before answering these questions!** After the lab, you will have the opportunity to re-think your ideas and give us more elaborate thoughts. Read information in the text related to the topic.

Experimental procedure: Describe the experimental procedure in *your own* words (on another sheet). You may use any method you like such as bullet points or diagrams. Be *brief* but clear as this will be the procedure you will use to perform the experiment. You will not be allowed to use the experiment handout during the lab. Describe completely in this procedure the steps you will perform for each reaction to observe equilibrium. Since you do not know the reagents ahead of time, describe what types of chemicals or reagents could be used to accomplish these shifts. You should note the expected sensorial observations resulting from your changes.

Pre-lab Thoughts

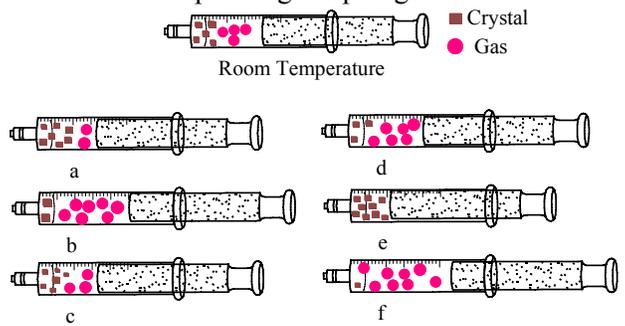
1) a) Complete the following diagram (fill in the blanks) using the word list to form the definition of equilibrium.



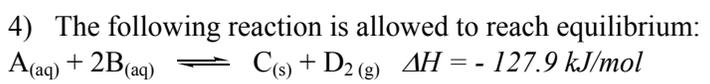
b) Briefly explain in your own words the completed (**bolded**) pathway.

2) You are given a closed jar containing a blue liquid and observe the liquid evaporates making the air in the jar *saturated* (increased concentration) with a blue vapor above the liquid. You observe that the vapor condenses on the top of the jar and drips back into the liquid. You cleverly manipulate the *extent* of these observations by warming or cooling the jar and observe at a certain constant temperature no more changes occur. However, your instructor tells you that the *extent of evaporation is now equal to the extent of condensation!* Based on the data, in your own words, define dynamic equilibrium. Draw diagrams to represent molecularly what happens in the closed jar at dynamic equilibrium.

- 3) Brown crystals are heated in a closed syringe and sublimates to a pink gas that pushes against the plunger. The gas is cooled causing crystals to reform. When left to reach room temperature, both crystals and gas are observed with no observable changes occurring.
- Write an equilibrium equation representing the description.
 - Choose all possible scenarios that result from decreasing the volume, i.e. pressing the plunger.

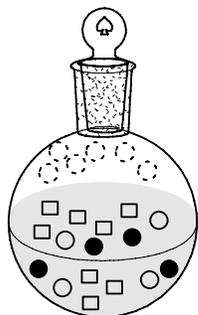


Equilibrium equation:



What will be the overall effect on the concentrations of products or reactants when the reaction is allowed to *re-achieve equilibrium* if:

- gas D_2 is burned
- HCl is added to the system and HCl reacts with B



A ○
 B ●
 C □
 D₂ ⊙
 At equilibrium

c) C is filtered out of the system

d) the temperature is increased

Demonstrate each change pictorially.

<p>a) gas, D₂, is burned (consumed)?</p>	<p>b) HCl is added to the system, and HCl reacts with B?</p>
<p>c) C is filtered out of the system?</p>	<p>d) the temperature is increased?</p>

5) a) Classify the following into either chemical or physical change: sublimation, dissolve salt, neutralize acid, melt ice, crystallization, evaporation, cooking egg, condensation, boiling water, burned toast, nail rusting, freezing liquid, and souring milk.

b) Choose one item from each group; depict pictorially the transformation occurring at the molecular level and explain the change. Discuss what distinguishes the classification.

c) Draw a concept map linking the following terms to chemical and physical changes and include the following words: equilibrium, reversible, temperature, substance change, molecular reaction, irreversible, reactants, bond making, intermolecular forces, phase change, state.

i) Classify: Physical change	Chemical change
ii) Depict: Physical change:	Chemical change:
iii) Concept map:	

Equilibrium and Applications of Le Chatelier's Principle

Introduction:

Various factors may affect the dynamic equilibrium of a reaction under specific conditions. Typically, equilibrium experiments are monitored by visual changes. In this experiment, you will explore visual as well as other sensorial changes that occur in a variety of reactions. You are required to decide on your own what factors affect the reaction and would affect the concentration of the products and reactants.

Warning:

Strong acids and bases are corrosive and may cause burns. Chromium is toxic. Ammonia and butylamine have strong odors; do not inhale directly. Extreme care must be taken when using these chemicals. Follow instructions on their use given by your instructor. Treat all chemicals as hazardous, and avoid contact with your skin. Consult instructor about chemical spills and burns. Inhaling any compound too long or directly could be irritable and/or hazardous. Always waft aromas.

Procedure:

You will work in groups of 2-3 students. The experiment is divided into stations (A-G) with all the necessary reagents for that reaction provided. Manipulate the reactions in order to affect the concentration of the products ([prod]) or reactants ([react]) by influencing the equilibrium, noting the *extent* of any changes. Indicator solutions are used to detect acids (H^+ species) or bases (OH^-) in this experiment. You are required to use all the chemicals and equipment available at each workstation to decide the path needed to observe Le Chatelier's principle. Write all procedures and observations in your lab notebook using *all your senses* and being as descriptive as possible.

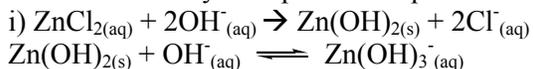
In order to perturb the equilibrium, determine what will increase the [prod] and [react] in the solution, and perform this reaction. Shake the test tube thoroughly to allow for mixing. *Use only 1 drop of any indicator solution and do not use more than ~10 drops of any solution*, unless otherwise told by your instructor. Once you have completed each part, clean the test tubes with soap and water. Clean-up the workstation for the next group. Work in a timely fashion. Record the results in a table similar to Table 1 including reagents added and any necessary information. Record *all observations* including smell, sound, color changes and precipitate formation.

Table 1. Sample data table

Procedure	Example: $A_{(s)} + B_{(l)} \rightleftharpoons C_{(l)} + D_{(g)} \quad \Delta H = + 20 \text{ kJ/mol}$			
	Sensorial Observations			
	Smell	See	Hear	Feel
Added A and B to test tube	Flowery smell	Blue solid dissolved to form a clear solution	Popping sound from test tube; Rapid beeping sound	Slightly cold tube
Added 10 drops C to test tube	No smell	Clear solution to blue solid in clear liquid	No sounds heard from test tube; decreased beeping sound of light probe	Warm tube
Remove some B by filtering	No smell	Blue solid slowly reformed in clear liquid	No change	Slightly cold tube
Heated test tube for 5 minutes	Flowery smell	Blue solid dissolved to form a clear solution	Popping sound from test tube; Rapid beeping sound	Hot from heating

Each equilibrium reaction you perform falls under a category, which describes the type of equilibria that the reaction exhibits. Be certain that you understand these categories related to the equilibria you are studying.

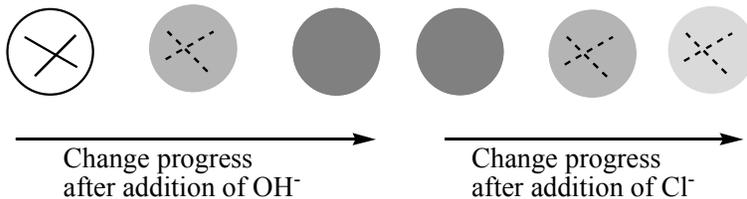
Part A. Solubility/Complex Ion Equilibria



Dissolving Precipitates

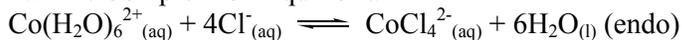


Discussion Part A: If you placed an 'X' on a sheet of paper under your test tube and viewed it from above you may have observed the following:



- How would you describe your concentrations of $BaCl_2$, and $Ba(OH)_2$ for each?
- Was this a chemical or physical change? Why?

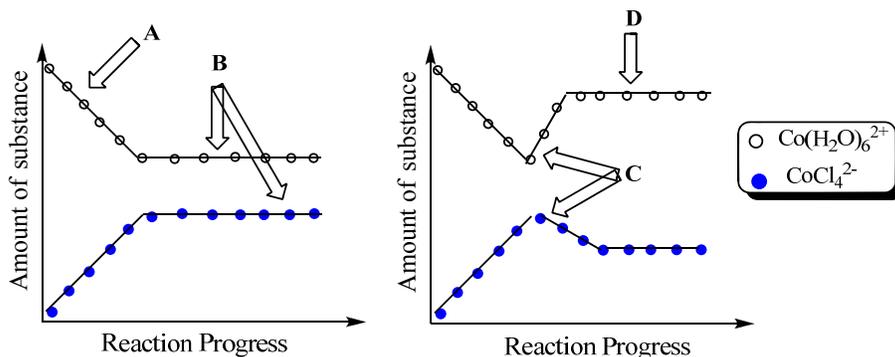
Part B: Complex Ion Equilibria



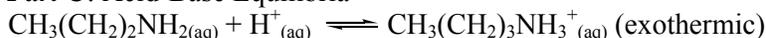
Note: Do not smell Conc. HCl. Add *drop-wise* to observe more than 2 colors (light probe: multiple frequency changes).

Discussion Part B:

- How could you determine the extent of this reaction (degree of formation of reactants and products) and when dynamic equilibrium is taking place (based on your data)?
- Explain what is occurring in the test tube for the reaction in Part B depicted in the graphs below. Explain what is occurring at the areas labeled A-D in the reaction, and discuss the changes in [prod] and [react].



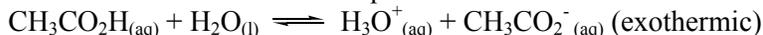
Part C: Acid-Base Equilibria



Discussion Part C:

- What would be the K_{eq} expression for this reaction?
- If K_{eq} is a large value, how does this affect the concentrations of $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$ and $\text{CH}_3(\text{CH}_2)_3\text{NH}_3^+$?
- You were given the expression $K_{\text{eq}} = e^{(\Delta G / -RT)}$. Knowing that ΔG and R are constant values for this reaction, briefly explain how you would determine K_{eq} using this equation.

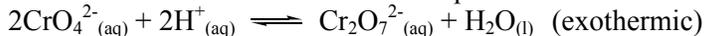
Part D: Common Ion Effect Equilibria



Discussion Part D:

- Based on your experiments, what tests have you performed in order to observe the *common ion effect* (include your definition of the term in your explanation)?
- In order to achieve this with an acid or base, what criterion is critical about the acid or base for the reaction to exhibit a common ion effect? Explain this in terms of equilibrium.

Part E: Chromate acid-Dichromate Equilibria



Discussion Part E:

- Draw *concentration vs. reaction progress graphs* to represent your observations in Part E.
- Indicate on your graph what is occurring. If you slightly dehydrated your reaction (removed water from your reaction at equilibrium), how would it change your graph? Draw a new graph to reflect the water removal.

Part F: Solubility-Equilibria (with temperature dependence)



Discussion Part F:

- $\text{NH}_4\text{Cl}_{(aq)}$ is a *saturated* solution. Describe the dynamic equilibrium occurring in this solution and represent this pictorially in a diagram.
- If you performed this experiment with extreme temperatures such as those in Antarctica or the Sahara desert, how would the temperature affect the [prod] and [react]?

Part G: Equilibria to be explored (only one will be assigned to you):

- $\text{CuCl}_2_{(aq)} + 2\text{OH}_{(aq)} \rightarrow \text{Cu}(\text{OH})_{2(s)} + 2\text{Cl}^-_{(aq)}$
 $\text{Cu}(\text{OH})_{2(s)} + \text{excess NH}_3_{(aq)} \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}_{(aq)} + 2\text{OH}^-_{(aq)}$
- $\text{Al}(\text{NO}_3)_3_{(aq)} + 3\text{OH}^-_{(aq)} \rightarrow \text{Al}(\text{OH})_3_{(s)} + 3\text{NO}_3^-_{(aq)}$
 $\text{Al}(\text{OH})_3_{(s)} + \text{excess OH}^-_{(aq)} \rightleftharpoons \text{Al}(\text{OH})_4^-_{(aq)}$
- $\text{HIn}_{(aq)} \rightleftharpoons \text{In}^-_{(aq)} + \text{H}^+_{(aq)}$
- $\text{NaNO}_3_{(s)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{NaNO}_3_{(aq)} \quad (\text{endothermic})$
- $\text{NH}_3_{(aq)} + \text{H}^+_{(aq)} \rightleftharpoons \text{NH}_4^+_{(aq)} \quad (\text{exothermic})$
- $\text{CaCl}_2_{(aq)} + 2\text{OH}^-_{(aq)} \rightleftharpoons \text{Ca}(\text{OH})_2_{(s)}$
- $\text{NH}_3 + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{OH}^-_{(aq)} \quad (\text{exothermic})$

Post-Lab Report:

Your report must be typed. Graphs and pictures may be drawn neatly by hand.

1) Results and discussion:

- Organize the results of your reactions in a table (similar to Table 1) showing what you changed in each case (procedure) and how it affected reactions. *Be specific but brief.*
- Discuss *each* sensorial observation **for each reaction** (in a) in terms of the chemical or physical changes that occurred (*be specific and clear*) and how it demonstrated changes in product and reactant concentrations. Answer the question clearly for each part (A-F).
- Assign your reaction in Part G a classification (e.g. Complex Ion, solubility, etc.). Briefly explain your classification (your reaction may fall into multiple groups).
- What other experiments could you have performed and what other chemicals would you have liked to have used?
 - How do you think this experiment can be improved? Explain your opinions
- What did you learned about equilibrium reactions, dynamic equilibrium and Le Chatelier's principle from this experiment?.

2) General questions:

- You are given the following in a *closed syringe*: $\text{N}_2\text{O}_4_{(g)} + \Delta \rightleftharpoons 2\text{NO}_2_{(g)}$
- What factors (inside and outside) would disrupt the equilibrium and to what extent would [prod] and [react] be affected by each?
- N_2O_4 is a colorless gas, and NO_2 is brown. What would you observe with these factors, and how can you determine experimentally that equilibrium has been established? Explain your answers using diagrams and graphs to represent what is taking place in the syringe.

vi) What do you expect will happen if you pulled the plunger of the syringe and increased the volume inside?

c) You are given the following reaction: $\text{CH}_3\text{CO}_2\text{CH}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{CO}_2\text{Na}(\text{aq}) + \text{CH}_3\text{OH}(\text{aq})$. You observe that when the reaction is placed on ice you observe a sweet smell dominating ($\text{CH}_3\text{CO}_2\text{CH}_3$). When you heat the reaction, you smell an increased alcohol aroma (CH_3OH).

i) After you heat, a compound that removes your base is added. What would you expect to occur? Pictorially depict all the changes and their effect on concentrations.

ii) Determine with a brief explanation whether the forward and reverse reactions are exothermic or endothermic from your observations.

3) Reflection:

Re-examine each question in your pre-lab thoughts. Have any of your original thoughts changed or been clarified? Explain: Why or why not? Be specific! *Additionally, you must re-answer all questions which your instructor indicated were incorrect or incomplete.*

4) Conclusion:

a) Summarize your ideas in order to show what factors can affect concentration changes in a chemical equilibrium, and comment how it could be useful in everyday life.

b) Devise a *reasonable* question related to this experiment (different from the post-lab questions) and give a plausible answer.

Equilibrium Instructor's Notes

Purpose: Typical Le Chatelier experiments involve reactions that show changes in color or states of matter to demonstrate the principle of equilibrium. This experiment involves reactions that not only demonstrate color and state changes, but also add temperature and olfactory changes. These experiments utilize multiple senses to make chemical determinations. Students with visual disabilities will be able to monitor the chemical changes along with their classmates. The visual changes in the experiment are carefully chosen to be also detected with the use of a light probe.

This experiment is written as an inquiry-based laboratory. Students are required to decide on their own what factors affect the concentration of the products and reactants. It is important that the students not waste time and resources, and hence not perform unnecessary tests.

Reagents used (CAS numbers):

Hydrochloric acid - 7647-01-0	Potassium Dichromate - 7778-50-9
Sodium hydroxide - 1310-73-2	Cupric Chloride – 10125-13-0
Zinc chloride – 7646-85-7	Aluminum Nitrate – 13473-90-0
Barium chloride – 10326-27-9	Cobalt Chloride – 7791-13-1
Sodium Acetate trihydrate - 6131-90-4	Calcium chloride dihydrate – 10035-04-8
Ammonium chloride - 12125-02-9	Methyl Red- 63451-28-5
Acetic Acid - 64-19-7	Phenolphthalein - 77-09-8
Propylamine - 107-10-8	Potassium chromate – 497-19-8
Ethyl Acetate - 141-78-6	Sodium carbonate - 7789-00-6

Lumitest light probe - American Printing House for the Blind Inc., Louisville KY.
Ammonia (Household)

Directions for making reagents (~60 students):

Liquid: In a volumetric flask, add slowly to half the required deionized water. Swirl the solution slightly and add remaining deionized water to fill the flask to the mark. Shake the solution until completely mixed.

Solid: Place solid in the volumetric flask and add deionized water to fill the flask to the mark. Shake the solution until completely mixed.

Phenolphthalein solution: 0.05g of phenolphthalein is placed in 50 mL of deionized water. To this solution, 50 mL of ethanol is added.

Table D.1. Chemicals and quantities needed for equilibrium experiment.

Solution	MW/Concentration	Mass/Volume	Volume made
<i>6.0 M Hydrochloric acid</i>	12.1N	99.2 mL	200.0mL
<i>0.2 M Acetic acid</i>	60.05g/mL	0.7 mL	60.0mL
<i>1.0 M 1-propylamine</i>	59.1g/mol, 0.7g/mL	0.9 mL	10.0mL
<i>6.0 M Sodium hydroxide</i>	40.00g/mol	72.000g	300.0mL
<i>Phenolphthalein solution</i>		0.05g	100.0mL
<i>0.5M Aluminum nitrate solution</i>	212.9962 g/mol	1.597g	15.0mL
<i>1.0M Sodium acetate solution</i>	136.08 g/mol	13.608g	200.0mL
<i>0.5M Zinc chloride solution</i>	136.29 g/mol	4.089g	60.0mL
<i>0.5M Cupric chloride solution</i>	170.48g/mol	1.279g	15.0mL
<i>0.5M Potassium dichromate solution</i>	294.19 g/mol	8.826 g	60.0mL
<i>0.5M Barium chloride solution</i>	244.27g/mol	7.328g	60.0mL
<i>0.5M Calcium chloride solution</i>	147.02/mol	0.735g	10.0mL
<i>0.5M Cobalt chloride</i>	237.93g/mol	7.138g	60.0mL
<i>6.0M Sulfuric acid</i>	18N	66.7mL	200.mL
<i>3.0M Sodium carbonate</i>	105.99 g/mol	47.696g	150.mL
<i>0.5M Potassium chromate</i>	194.19g/mol	5.826g	60.0mL
<i>0.5M Ammonium chloride</i>		~1g	

0.2 M Acetic acid alternative: Pure vinegar diluted to about 0.2M acetic acid.

Ammonia Alternative: Household ammonia.

All acidic reagents are placed in glass dropper bottles and all other reagents are placed in plastic dropper bottles. The dropper bottles are used to reduce contamination of the reagents. The bottles should be kept tightly closed.

Hazards:

The use of strong acids may cause skin burns. It is advised that these acid solutions be prepared in the hood. Bases are corrosive and may cause burns. Students should wear standard laboratory gear such as goggles, closed-toed shoes, and clothing that covers the torso and legs. Students should waft the chemicals.

Suggestions and Notes:

General Instruction

- The experiment is an inquiry-based laboratory and requires students to decide on their own what needs to be done in order to proceed. Students may be given hints only if they need to perform further testing to complete the experiment.
- Student groups should be timed at each station to prevent a station from being occupied too long. Each group may be assigned an equilibrium reaction to begin with and the order in which to proceed. For example, Group 1 may be asked to start with Part B then proceed to C then D, while another starts with C and proceeds to D.
- The results of the light probe may depend on the light probe used. The results obtained in this experiment are based on the Lumitest light probe. Other light probes may show the difference between colors, however, will cost significantly more than a probe that detects only changes in light intensity.
- For students using the light probe, let them test how the probe works and the different frequencies it emits. Have a variety of test tubes set-up with a range of colors from clear to opaque, so the students can spend a couple of minutes using these probes and familiarize themselves with the sounds. Have the light probe instructions available to the student before and during the lab.

Set-up

- Solids may be pre-weighted and placed at the station in test tubes for the students to use rather than having them weigh the solids.
- Waste containers for each reaction must be set-up next to the experiment along with any necessary cleaning items.
- For large enrollment labs, multiple stations for each reaction may be set-up simultaneously.

Experiment

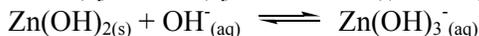
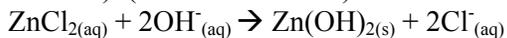
- Students should not use more than a drop of indicator solution as these may have an alcoholic smell that may distort the observations if used in excess.
- Students may be instructed as to how many drops may be too many, but as an inquiry experiment, they must try to find the answers on their own. In many cases, the students can be instructed not to use more than 10 drops of any solution or ~1g of any solid, therefore minimizing waste.
- Indicator (HIn) for Part G reaction may be any acid-base indicator. Phenolphthalein was used in this experiment.

Sensory precautions and suggestions

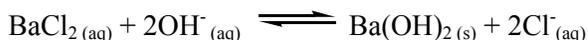
- Demonstrate the method of proper wafting to the students and ensure this is the method they use to perceive aromas.
- Students must not smell anything containing conc. HCl.
- Coffee crystals can be made available for the students to smell between stations. This is a recommended procedure to “clean” the sense of smell. Some students took advantage of this while others didn’t think it was necessary.
- Students may observe the reactions by touch, but ensure that they do not have contact with any reagent directly. They should observe temperature changes through the test tubes only.
- Students must not taste anything or put anything in the lab into their mouths.

These are a sample of the suggested labels to be placed with each reaction set-up (the labels should be enlarged).

Part A i). (Time: 10 minutes)



Part A ii) (Time: 5 minutes)

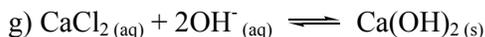
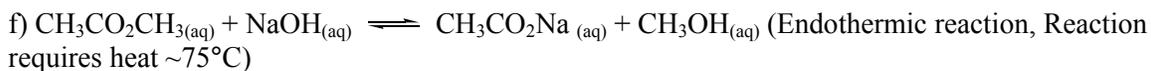
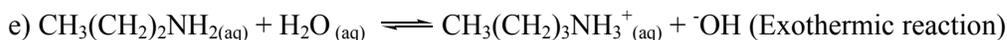
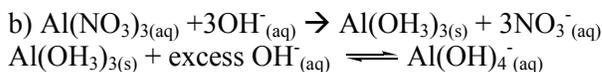
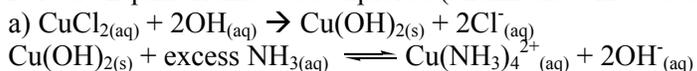


Part B: (Time: 15 minutes)



NOTE: DO NOT SMELL CONC. HCL.

Part G: Equilibriums to be explored (chemicals will be assigned):



Additional student data and Rubric Sample Responses

Although students still used incorrect terminology, their Responses provided were insightful. More emphasis needs to be placed on the instructors to use correct terminology in any assistance or guidance provided to the students to prevent the use of incorrect terminology.

Generic or text-book related Post-lab Question 5 responses (C responses):

“The equation above is one that can follow Le Chatelier’s Principles. Changes in total pressure and volume, for example, [they] could shift this reaction to one side or the other, depending on those two variables.”

“The factors that affect the reaction flask are pressure outside the flask and inside the flask is the concentration. The pressure will affect the reaction by changing the way the reaction takes place until it reaches equilibrium.”

Thoughtful Post-lab Question 5 response (C&C):

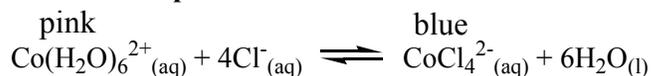
“In the reaction, $\text{N}_2\text{O}_{4(g)} \leftrightarrow 2\text{NO}_{2(g)}$, the factors inside and outside of the flask that would affect the equilibrium of this reaction would be adding or removing elements, changing temperature, and changing the volume or pressure of the flask. Adding N_2O_4 would shift the equilibrium towards the right because there would exist more molecules on the left side of the reaction, causing the reaction to move in order to achieve equilibrium. Also, adding NO would shift the equilibrium to the left because there would be more molecules on the right side, so the reaction will increase the other side to achieve equilibrium. Also, increasing the volume decreases the pressure. This will shift the equilibrium to the right because there are more molecules on the left side and more gas molecules are produced. Also, increasing the temperature would affect the equilibrium of the reaction by shifting the equilibrium to the right. By decreasing the temperature, the equilibrium would be shifted to the left. Adding a catalyst will never be a factor that affects the equilibrium of a reaction. It would only decrease the activation energy.”

Students thought critically about the experiment as shown through LLR format through examining further experimentation, mistakes made, what was learned, conclusions drawn or comparisons drawn to examples in everyday life. Some students’ responses to these areas:

- “If we had CoCl_4^{2-} , we would have added that after we already added HCl to cause more reactant to form.”
- “From this experiment, I learned heating an endothermic reaction had the same effect as adding reactants to it.”
- “There is an equilibrium between our blood, specifically the hemoglobin and the oxygen of the blood and muscle.”

Table D.2. Number of students with complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N) in the equilibrium pre-lab questions.

Section		Points	Average	C&C	C	SC	N
Part Ai	Detailed procedure	2	66%	31%	69%	0%	0%
	Sensorial results	2	62%	24%	76%	0%	0%
Part Aii	Detailed procedure	2	68%	36%	64%	0%	0%
	Sensorial results	2	64%	29%	71%	0%	0%
Part B	Detailed procedure	4	73%	60%	36%	4%	0%
	Sensorial results	4	71%	60%	29%	11%	0%
Part C	Detailed procedure	3	85%	62%	31%	7%	0%
	Sensorial results	3	83%	62%	24%	13%	0%
Part D	Detailed procedure	3	74%	40%	44%	13%	2%
	Sensorial results	3	71%	36%	44%	18%	2%
Part E	Detailed procedure	3	84%	53%	44%	2%	0%
	Sensorial results	3	81%	53%	38%	9%	0%
Part F	Detailed procedure	3	87%	67%	29%	4%	0%
	Sensorial results	3	81%	62%	20%	18%	0%
Part G	Detailed procedure	2	88%	73%	27%	0%	0%
	Sensorial results	2	84%	67%	33%	0%	0%
1	Other experiments	7	22%	16%	9%	0%	76%
2	Classify new reaction	1	58%	58%	0%	0%	42%
a. Discussion	Part Ai	2	61%	33%	56%	0%	11%
	Part Aii	2	61%	33%	56%	0%	11%
	Part B	2	60%	33%	53%	0%	13%
	Part C	2	67%	44%	44%	0%	11%
	Part D	2	69%	49%	40%	0%	11%
	Part E	2	68%	49%	38%	0%	13%
	Part F	2	67%	47%	40%	0%	13%
b	Factors that affect: $\text{N}_2\text{O}_4_{(g)} \rightleftharpoons 2\text{NO}_2_{(g)} + \Delta$	4	60%	42%	33%	18%	7%
c	Non-text book definition and critical criteria of common ion effect.	3	76%	60%	20%	9%	11%
d	Non-text book definition and use of complex ion.	2	71%	58%	27%	0%	16%
Conclusion	Concise	8	77%	64%	31%	0%	4%

Additional experimental data

Procedure: 2.0 mL of the cobalt solution was added to test tubes containing the weighed mass of each salt. The test tubes were shaken and observed for 5 minutes. Color changes and the degree of dissolution were noted. These tubes were then heated for at most 5 minutes in a water bath at 79.5°C. The test tubes were periodically shaken. Color changes and the degree of dissolution were noted.

Possible future experimentation: Aluminum, chromium, and beryllium chlorides; Observe row trends/periodic, compare lability, hydrates vs. anhydrous, concentration, concentration of HCl, molecular sieves, solubility.

Table D.3. Complete chloride source investigation data.

Chloride	Mass, g	Conc, M	solubility, g/100mL	Ambient	Heated
NH ₄ Cl	0.52	4.86	39.5	No color change (pink), cold	Quickly turns from pink to blue
KCl	0.50	3.35	34.00	No color change (pink), cold	slowly turns from pink to pink-purple
BaCl ₂ ·2H ₂ O	0.52	1.06	37.00	Pink to a light pink-purple	No color change (light pink-purple)
MgCl ₂ ·6H ₂ O	0.55	1.35	56	No color change (pink), cold	Pink to a pink-purple
CaCl ₂ ·2H ₂ O	0.50	1.70	81.3	No color change (pink), cold	Pink to a light pink-purple
MnCl ₂ ·4H ₂ O	0.52	1.31	77.3	No color change (pink), cold	No color change (pink)
CaCl ₂	0.51	2.30	81.3	Pink to a light pink-purple, warm	instantly turns from pink to dark blue
CuCl ₂	0.53	1.55	75.7	Dark blue (Co)	Cobalt blue to copper Green to dark green
ZnCl ₂	0.53	1.94	408	No color change (pink), warm	No color change (pink)
NH ₄ Cl	1.03	9.63	39.5	No color change (pink), cold	instantly turns from pink to dark blue, incomplete dissolution
KCl	1.03	6.91	34.00	No color change (pink), cold	Pink to Blue
BaCl ₂ ·2H ₂ O	1.07	2.19	37.00	No color change (pink), cold	pink to very light purple, incomplete dissolution

Table D.3. Complete chloride source investigation data (continued).

Chloride	Mass, g	Conc, M	solubility, g/100mL	Ambient	Heated
MgCl ₂ ·6H ₂ O	1.02	2.51	56	Pink to light pink-purple, cool	light pink-purple to pink-purple then light purple
CaCl ₂ ·2H ₂ O	1.03	3.50	81.3	No color change (pink), cold	pink to purple, then blue-purple
MnCl ₂ ·4H ₂ O	1.04	2.63	77.3	No color change (pink), cold	pink to very light purple
CaCl ₂	1.04	4.69	81.3	Pink to Blue, hot	Blue to Dark blue
MgCl ₂	1.01	5.30	56.2	Pink to Blue, hot	Blue to Dark blue
ZnCl ₂	1.02	3.74	75.7	No color change (pink), warm	No color change (pink)
NH ₄ Cl	1.96	18.32	39.5	No color change (pink), cold	Pink to dark purple then blue, incomplete dissolution
NaCl	2.00	17.11	36.5	No color change (pink), cold	Pink to dark purple then blue, incomplete dissolution
KCl	2.04	13.41	34.00	No color change (pink), cold	Pink to dark purple then blue, incomplete dissolution
BaCl ₂ ·2H ₂ O	2.06	4.18	37.50	No color change (pink), cold	pink to light purple
ZnCl ₂	2.09	7.63	75.7	No color change (pink), warm	No color change (pink)

Table D.4. Common drying agents' strength and power of dehydration.

Drying agent	Dehydration power (strength)	Rate of dehydration
CaCl ₂ (anhydrous)	high	medium
CaSO ₄ (Drierite)	low	fast
K ₂ CO ₃ (anhydrous)	medium	medium
MgSO ₄ (anhydrous)	high	fast
Molecular sieves	high	fast
Na ₂ SO ₄ (anhydrous)	high	slow
Silica gel	high	fast

Appendix E. Acetyl salicylic Acid Kinetics Experiment

Acetylsalicylic Acid Kinetics Pre-lab

Experimental procedure:

You will not be allowed to use the experimental procedure handout in the lab. Your experimental procedure must be checked by your instructor before you can perform the experiment. Your pre-lab and procedure should include:

1. Briefly **outline** your experimental and learning objectives. What is the question you will be answering or exploring in the lab? What do you expect to learn from this experiment?
2. **Describe** the experimental procedure in your *own* words. You may use any method you like such as bullet points or diagrams. Be brief, but clear as this will be the procedure you will use to perform the experiment.
3. Determine what experimental data will be collected and what information must be calculated (Pre-lab question 4a).
4. Be able to draw typical kinetics graphs and understand how graphs are used in kinetics experiments to distinguish between different rate orders and derive rate constants (see pre-lab question 3).
5. What do you expect the outcome of your experiment will be?

Name: _____ Lab section: _____ Lecture table #: _____
 T.A.: _____ Group: _____ Date: _____

Pre-lab Questions:

These pre-lab questions **must** be completed before the lab and turned to the instructor on the date announced. **Read the entire experiment before answering these questions!** After the lab, you will have the opportunity to re-evaluate your responses and give the correct and more elaborate responses to earn lost points only for questions for which you make an honest attempt to answer the question.

1. a) Your friend only speaks the language of 'Chemistry' and tried to translate a rate of reaction lecture with some difficulty. You help your friend by filling in the blanks. Use your textbook as a 'Chemistry' dictionary.

<p style="text-align: center;"><u>Chemistry translation</u></p> <p style="text-align: center;">$aA + bB \longrightarrow cC + dD$</p> <p style="text-align: center;">..... products</p>	\Longrightarrow	<p style="text-align: center;"><u>Terminology</u></p> <p>Chemistry equation representing the reaction of A & B to form the products, where a, b, c and d are stoichiometric</p>
<p style="text-align: center;">$\text{Rate} = \frac{-\Delta[A]}{a\Delta t}$</p> <p style="text-align: center;"><i>Expression A</i></p> <div style="border: 1px solid black; border-radius: 10px; padding: 5px; width: fit-content; margin: 10px auto;"> Rate expressions may take two forms </div> <p style="text-align: center;">$\text{Rate} = k[A]^x[B]^y$</p> <p style="text-align: center;"><i>Expression B</i></p>	<p style="text-align: center;">\Longrightarrow</p> <p>Rate of reaction is the in a reactant concentration of A per mole over the in time. Δ symbolizes (same word for the 3 blanks)</p>	
<p>rate order =</p> <p>... - order with respect to [A]</p> <p>... - order with respect to [B]</p>	<p style="text-align: center;">\Longrightarrow</p> <p>Rate expressions A and B are dependent on Expression A is related to the of A by time. Expression B, the rate law, is related to the of A & B by k, the (3 of the blanks are the same word)</p>	
<p>.....</p>	<p style="text-align: center;">\Longrightarrow</p> <p>Overall rate order is the sum of the powers of all the reactants in the rate law.</p>	

b) What determines the **exponents** of the rate law? Select the correct response below.

i)experiments	iv)all of the above
ii)coefficients in a balanced equation	v)only i and ii
iii)initial concentrations of a reactants	

c) Explain the difference between symbols 'a, b, c and d' and 'x and y' used in the diagram, stating how each is used and where they are generally placed?

a, b, c and d:

x and y:

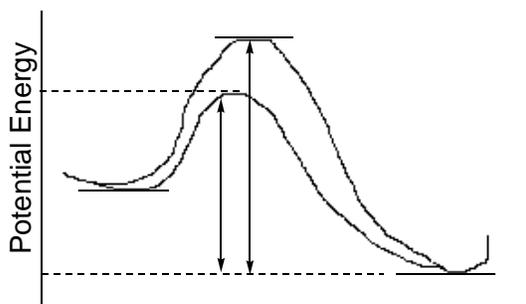
d) What is the rate law equation for your experiment using x and y as orders with respect to reactant concentrations?

Rate = _____

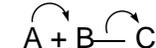
2. a) Define bimolecular reaction. How does this apply to the ASA hydrolysis?

The potential energy diagram below represents the energy changes that take place in a reaction scheme for a catalyzed and uncatalyzed reaction.

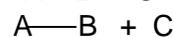
b) Using the labels below, indicate clearly on the diagram the reactants, transition state, products, catalyzed and uncatalyzed reaction. Match the labels with corresponding meaning.



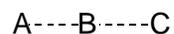
Use the following labels Match labels to words



Products



Transition state



Reactants

E_{act} - catalyzed

E_{act} - uncatalyzed

c) Is this an exothermic or endothermic reaction? Explain briefly including the enthalpy signs.

Exothermic / endothermic (circle one)

ΔH sign: _____

Explanation:

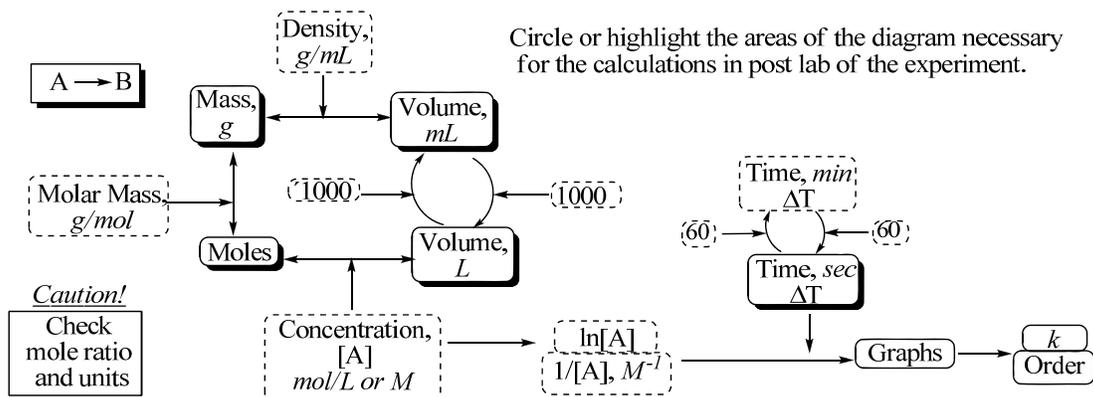
3. Fill in the blanks for the equations and graphs below to derive the kinetics equations.

	$\text{A} \longrightarrow \text{B}$		
	First Order $[A]^1 = [A]$		
<p>1 Simplify</p> <p>2 Rearrange</p> <p>3 Integrate</p> <p>4 Rearrange to express as a line equation</p> <p>5 Express as a graph with units</p>	$\text{rate} = k[A]^1 = \frac{-\Delta[A]}{\Delta t}$ $k = \frac{-\Delta[A]}{\Delta t}$ $k\Delta t = -\Delta[A]$ $\int k\Delta t = \int -\Delta[A]$ $kt = \dots + [A]_0$ $[A] = \dots + [A]_0$ $y = m x + c$	$\text{rate} = k[A]^1 = \frac{-\Delta[A]}{\Delta t}$ $k\Delta t = \dots$ $\int k\Delta t = \int \frac{-\Delta[A]}{[A]}$ $kt = \dots + \dots$ $\dots = -k t + \ln[A]_0$ $y = m x + c$	<p>Second Order</p> $\text{rate} = k[A]^2 = \frac{-\Delta[A]}{\Delta t}$ $k[A]^2 = \dots$ $\dots = \frac{-\Delta[A]}{[A]^2}$ $\int k\Delta t = \int -[A]^{-2} \Delta[A]$ $\dots = \frac{1}{[A]} + \frac{1}{[A]_0}$ $\frac{1}{[A]} = \dots + \dots$ $y = m x + c$
	$\int \frac{dx}{x} = \ln x + c$	$\int x^n dx = \frac{x^{n+1}}{n+1} + c$	

note: x & y are the measurable values, c is a constant and the intercept of graph (at $t=0$ sec)
 Integration: removes differential (Δ)

$\Delta[A] = d[A]$ $\frac{1}{x} = x^{-1}$
 $\int k dt = kt$

4. a)



b) In a kinetics experiment, you share data with other groups. However, the other groups did not collect data you could trust. Your instructor tells you the data you collected is enough to complete the table below. Calculate the values to **complete** the table below. You may use the diagram above. Show the calculations for the boxes numbered a-d!

A → B MM of A = 50.0g/mol
Volume of a = 200.0mL

Mass of A, g	moles of A	[A], M	ln[A]	1/[A], M ⁻¹	Time, sec
	0.20	1.00	0.00		60
15.00	<i>a</i>	1.50		0.67	50
20.00	<i>b</i>		0.69		40
<i>c</i>	0.50	<i>d</i>		0.40	30

Calculations (use correct significant figures and units)

<i>a</i>	<i>b</i>
<i>c</i>	<i>d</i>

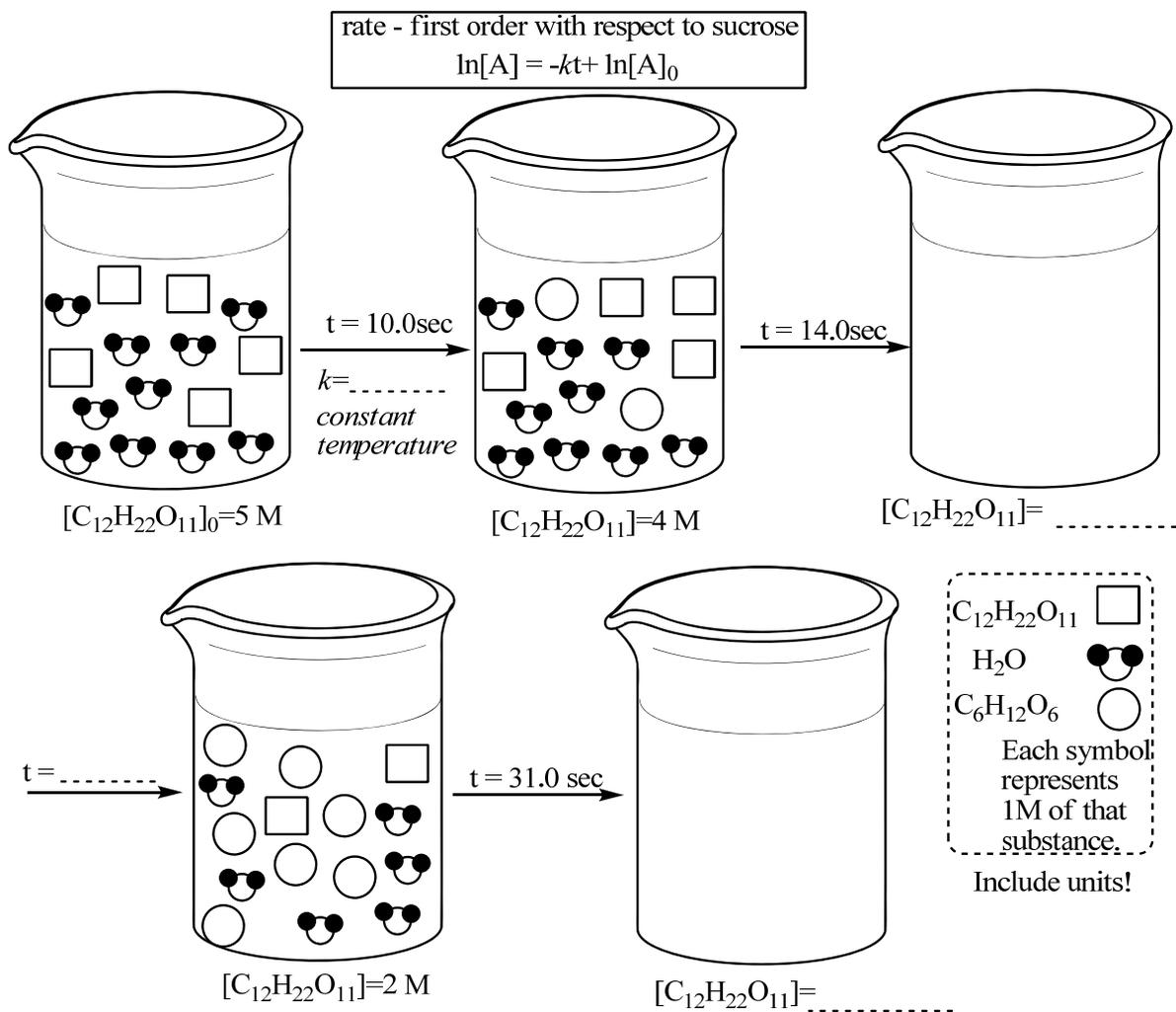
5. a) Balance the reaction below for the hydrolysis of sucrose, C₁₂H₂₂O₁₁.



b) The hydrolysis is *second order with respect to water* and *first order with respect to sucrose*. Represent this as a rate law and give the overall rate order (Show/explain how you got this number).

Rate law equation _____ Overall rate order _____ Does this rate law have any relationship to the numbers used to balance the equation above? Yes / No (circle one) Why?
c) Sucrose is hydrolyzed with excess water in order to monitor the rate with respect to sucrose. How does your rate law and the overall rate order change? How could you experimentally investigate this information and what data would you need to collect? New rate law equation _____ New overall rate order _____ Why? Experiment: Data to collect:

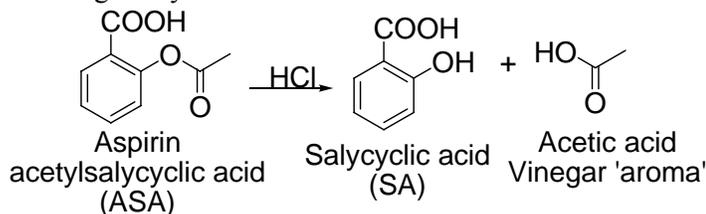
d) **Complete** the diagram and calculate concentrations, time and k . **Show all calculations**. Round up $[C_{12}H_{22}O_{11}]$ in increments >0.5 and round down for increments <0.5 .



What do you observe about the time as the reaction proceeds? Referring the **rate expressions** in *pre-lab question 1* and your *diagram above*, how does *rate change with time*? How could you prove your answer in the laboratory (be specific)?

Aspirin Kinetics

Introduction: In kinetic experiments we observe the effects of variables such as concentration and temperature on the rate of the reaction. Hydrolysis is the reaction of a compound with water. Aspirin (acetylsalicylic acid) can be hydrolyzed catalytically with acid to produce salicylic acid and acetic acid. Typical aspirin hydrolysis experiments use spectroscopic methods to determine the concentration of the resulting salicylic acid.



Experimental Inquiry: You will monitor the vinegar aroma produced by the reaction to determine the kinetics of the reaction with respect to ASA. Utilizing excess HCl at constant temperature, you will observe the reaction to determine the rate order with respect to ASA and derive a rate constant for the reaction. Review the topics of kinetics and enthalpy in your text.

Warning: The hydrochloric acid is corrosive and may cause burns. Aspirin may be harmful to students with allergies to certain pain medications. Consult instructor about chemical spills and burns.

Procedure:

Part A. Varying Concentration of Aspirin:

(Time Limit: 90 minutes) Work efficiently in groups of 2-3.

1. Assemble the set-up as shown in Figure 1, positioning the fan above the beaker (i.e. it must be blowing directly above and *not on* the beaker). You **must** stand about **12 inches** away from the fan (use the markings on the bench) in the direction of the air flow.

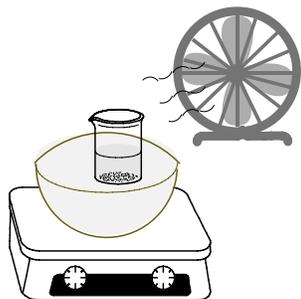


Figure 1. Set-up for kinetics study.

2. Fill the evaporation dish with water (about 3/4 full) and heat to about 65°C.
3. Measure 1.00 g of aspirin (acetylsalicylic acid or ASA) in a tared 50 mL beaker, recording the *actual weight* used. Try to weigh as close to the assigned weight as possible, but it does not need to be exact. You will be repeating this measurement in 1g increments. However, do not weigh all the samples at once.
4. Make a table similar to Table 1 to include 2 trials for each 1 g increment from 1.00 to 5.00 g.

Table 1. Sample ASA hydrolysis table. *Include all units!*

Mass	moles	[ASA]	T _i	T _f	ΔT	ln [ASA]	1/[ASA]
1.00g							
2.00g							

- Place a Teflon ® stir bar into the beaker, place the beaker into the water bath and allow stirring.
- Add 20.0 mL of M HCl to the beaker, turn on the fan and record the start time (T_i) in your table. **The final time (T_f) is the time at which the vinegar aroma is observed.**
- Continue observing the reaction for another ~30 seconds to ensure the aroma is persistent. *If the aroma goes away immediately, note the next time it is observed and persists (T_f is time aroma persists).*
- Repeat this procedure twice for each mass from **1.00 g to 5.00 g** in 1 g increments. If the resulting times for a specific mass are not within 10 seconds of each other, you should do an additional trial.
- Periodically measure the temperature of the bath to ensure that the bath is ~ 65°C, and keep the water bath ¾ full. Ensure that the reaction conditions are kept stable.
- If three trials were done and one value differs significantly from the other two, you may either repeat that mass if time permits or omit that trial (consult your TA). Include units in your table.

Part B. Clean up (10 minutes):

Turn off your hot plate, and allow to cool. Discard all organic waste in the corresponding waste container. Clean all beakers with soap and water.

Post-Lab Report:

Type or legibly write your responses to each section. Answer the general questions in the spaces provided. Graphs *must* be drawn with a graphing software program e.g. MS excel and diagrams may be drawn neatly by hand or an art program.

1) Results

Before leaving, the tables and graphs must be completed, inspected and signed by the TA. Return all data with your post-lab report. **Note:** *Each page submitted must have your name, date, partner name(s) and TA name.*

- Represent all data in tables similar to Table 1 using correct titles, labels and units.
- Show at least one mole, concentration and ΔT calculation including units and significant figures. Note: ΔT is the time taken for the aroma, T_f - T_i. You may refer to the calculation questions in the pre-lab or devise your own method of calculation, but *must* show the method used, demonstrating a *strategy* for how the values were calculated.

3. Draw the three *typical kinetics graphs* to explore rate order for each trial. *You may refer to pre-lab question 2.* Include on your graph the best fit or trend line and determine the line equation.
4. Compare the shapes of the *typical graphs* and explain what the shape of the graph implies about the reaction in order to establish the rate order with respect to ASA. *You may refer to pre-lab question 3 and post lab question 4.*
5. Using your answer in 4, determine the rate law and reaction order *with respect* to [ASA]. Using the graph that represents the rate order, determine the average rate constant, k , from the line of best fit.

2) Discussion

1. a) H^+ is considered a catalyst for the ASA hydrolysis. Draw an energy diagram to represent this reaction and the uncatalyzed reaction. Would you expect the products to be higher or lower in energy than the reactants? Why?
b) *Excess* $\text{HCl}_{(\text{aq})}$ was used in the experiment in order to observe a *pseudo reaction order* by monitoring only [ASA]. Suggest a method to determine the order of the reaction with respect to HCl?
2. Why is it important to keep the reaction conditions, particularly temperature, constant?
3. What are potential sources of error in this experiment (other than *incorrectly following the directions*)? What modifications could you suggest to remedy **these** errors?
4. Give a plausible reason why you were told not to measure all the ASA into all the beakers at once (other than the possibility of spilling)?
5. What other methods could be used to study the kinetics of this reaction?

3) Conclusion

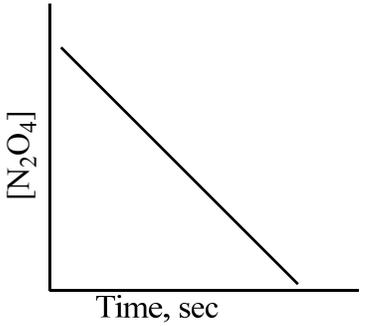
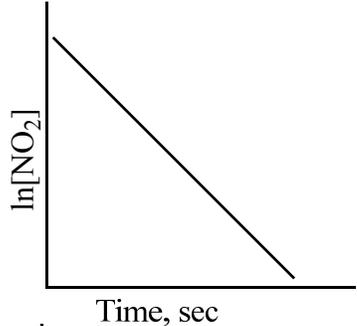
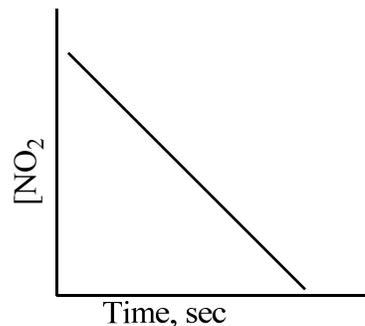
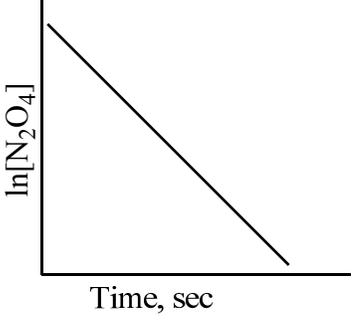
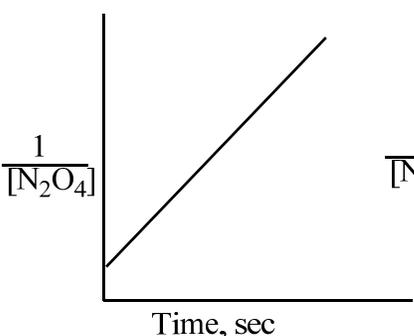
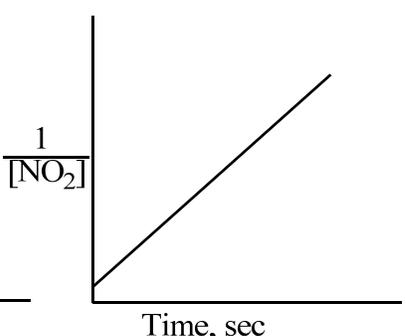
1. Summarize your findings on the hydrolysis of ASA.
2. Give a reason for using kinetics studies in the real/chemistry world (be specific).
3. Re-examine your pre-lab responses. Submit any changes or corrections to your original pre-lab on the sheet using a different color or attached to the original submission. How have any of your original thoughts changed or been clarified? Why or why not? **Be specific!**
4. Devise a *reasonable* question related to this experiment (different any pre and post-lab questions) and give a plausible answer. Be creative.

General Questions

Name: _____ Lab section: _____ Lecture table #: _____
 T.A.: _____ Group: _____ Date: _____

1. For $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$, the rate law is $k[\text{N}_2\text{O}_4]$.

Circle the graph that represents this information with a brief explanation. What are the units of k for the reaction?

		<p>Units?</p> <ul style="list-style-type: none"> i) $\text{M}^{-1}\text{s}^{-1}$ ii) Ms iii) s/M iv) M^2/s v) s^{-1}
		
		
<p>Explanation:</p>		

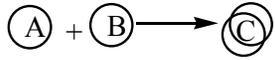
2. Using your experimental procedure as an example, give a *brief* explanation on a) what is meant by pseudo-first order reactions, b) how it is different from first order reactions and c) how is it different from second order reactions. You may explain your answer with the aid of diagrams and graphs.

a)

b)

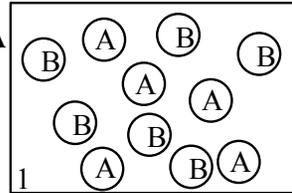
c)

3. Using appropriate chemical terminology and diagrams, you explain ballroom dancing to your friend who only speaks 'Chemistry'. You compare the effect of changing the speed of the music and increasing the number of people to increasing the temperature and concentration in a kinetics reaction respectively. a) **Complete** the diagram (boxes 3, 4 and 8), and calculate concentrations, time and k to *fill in the blanks*. **Show all calculations** on the diagram.



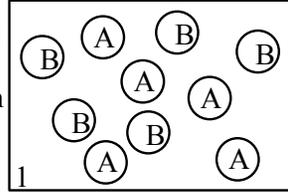
Rate law is $k[A]$
 $\ln[A] = -kt + \ln[A]_0$

Scenario A
 Conditions
 50°C , 1 atm
 $[A]_0 = 5 \text{ M}$

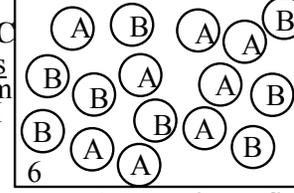


A & B enter the dance floor \approx
 A & B poured into a flask

Scenario B
 Conditions
 30°C , 1 atm
 $[A]_0 = 5 \text{ M}$

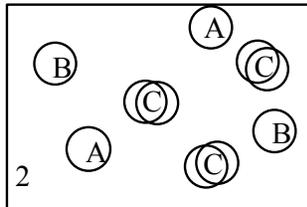


Scenario C
 Conditions
 30°C , 1 atm
 $[A]_0 = 8 \text{ M}$



More A enter dance floor \approx
 Increased, []

$t_1 = 10 \text{ sec}$
 $k = \dots \text{ s}^{-1}$



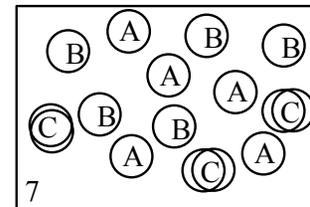
$[A] = 2 \text{ M}$

$k = 0.05 \text{ s}^{-1}$
 $t_1 = 10 \text{ sec}$



$[A] = \dots$

$k = 0.05 \text{ s}^{-1}$
 $t_1 = \dots \text{ sec}$



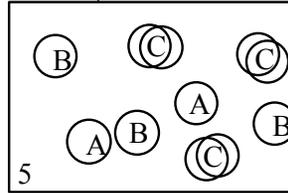
$[A] = 5 \text{ M}$

$t_2 = 10 \text{ sec}$



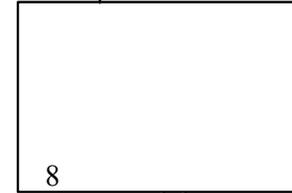
$[A] = \dots$

$t_2 = \dots \text{ sec}$



$[A] = 2 \text{ M}$

$t_2 = 18 \text{ sec}$



$[A] = \dots$

Faster music creates faster pace \approx
 temperature creates
 increased collisions of A
 compared to scenario B

k is dependent on
 and independent of

Larger crowd, but same pace \approx
 Increase A to form C, but
 same as scenario B

Notes: For $[A]$ in increments ≥ 0.5 round up and round down < 0.5

Each A represents 1 M

Include units!

b) Temperature affects E_{act} and the collisions between molecules. Referring to this statement, state how temperature impacts k and summarize your findings on the effect of temperature rate in the diagram in part a of this question?

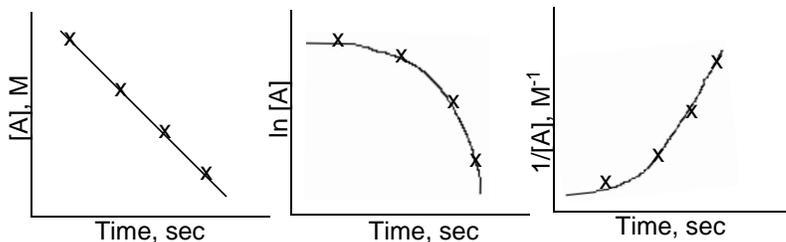
Temperature impact on k and rate:

In reference to E_{at} :

In reference to collisions:

4. The graphs below represent the kinetics data from *pre-lab question 4*. What **trends** do you notice with respect to $[A]$, $\ln[A]$, $1/[A]$ vs. **time**? Complete the blanks below to show the relationship between k and the slope as it relates to the integrated rate equations (refer to pre-lab question 3)?

Based on the graphs, what could you speculate about the rate order and why?



Rate order _____
Circle the graph used and explain briefly.

Trends

Slope:
negative/positive?

Since k is always >0 , based on the integrated rate equations:

For zero order, k is the _____ slope; rate equation: _____

For first order, k is the _____ slope; rate equation: _____

For second order, k is the _____ slope; rate equation: _____

Kinetics Instructor's Notes

Purpose: Acetylsalicylic acid (ASA) is the active ingredient in the common analgesic, aspirin, and the hydrolysis of which is commonly used in undergraduate chemistry kinetics experiments. This olfactory kinetics experiment allowed students to observe the vinegar aroma of acetic acid, noting the time taken to observe the aroma at various concentrations of ASA ([ASA]) and plotting their data in a similar manner as experiments performed spectroscopically. ASA hydrolysis kinetics experiments are typically studied spectroscopically. This experiment is written as an inquiry-based laboratory. Students are required to use their data to determine the rate order with respect to ASA and k .

Reagents used (CAS numbers):

Hydrochloric acid - 7647-01-0

Acetylsalicylic acid - 50-78-2

Items needed

Spatula	10 mL beakers	Clamp & Stand
Stir bar	Waste containers	Evaporation dish
Fan & 2 AA Batteries	Soap	Thermometer
50-100 mL beaker (waste collection container)	Hot plate	25-50 mL measuring- cylinder
	Paper towels	

Directions for 1 L of ~1.5M HCl (~20 students - 10 groups):

In a volumetric flask, add 124 mL concentrated HCl slowly to 500 mL deionized water. Swirl the solution slightly and add remaining deionized water to fill the flask to the 1000 mL mark. Shake the solution until completely mixed.

Hazards:

The use of strong acids may cause skin burns. It is advised that these acid solutions be prepared in the hood. Students should wear standard laboratory gear such as goggles, closed-toed shoes, and clothing that covers the torso and legs. Students should waft the chemicals.

Suggestions and Notes:

General Instruction and Experimentation

- The experiment is a guided inquiry laboratory and requires students to use their data on their own to determine the rate order with respect to ASA and k . Students may be given hints or assistance with MS EXCEL.
- Students should be warned as to the safety issues.
- Students should not use more HCl or ASA than needed for each trial.
- Students should conduct at least 2 trials.
- Stress to students to record the initial time they make their observations, then continue smelling for about 30 seconds to ensure the aroma does not go away.
- Remind students to clean up the lab benches and their hands with soap and water, as the ASA will not dissolve readily at room temperature.

Set-up

- Waste container should be set-up in the hood.
- Small waste collection should be placed at the students' bench and disposed of when full in the general waste container.

- The most likely sources of error are students not correctly placing the set-up ~12 inches away.
- The students must sit in the direction of airflow from the fan in order to accurately detect the aroma.
- It is very important that the temperature of the water bath is kept relatively constant during the reaction.
- You may attach markers on the bench to indicate the appropriate distance for the set-up (see suggestion below).

These are a sample of the suggested place markers to be placed with each reaction set-up (the labels should be enlarged to 30 cm).

↑ Fan here				
Observe aroma at this distance from fan!				
Stand here ↓	Stand here ↓	Stand here ↓	Stand here ↓	Stand here ↓

Sensory precautions and suggestions

- Various hand-held, portable or desk fans may be used. They must, however, be small enough to point primarily over the beaker as well as blow the air relatively weakly i.e. have a low setting.
- Allow the students to take breaks during the experiment.
- Coffee crystals can be made available for the students to smell between stations. This is a recommended procedure to “clean” the sense of smell. Some students took advantage of this while others didn’t think it was necessary.
- Students must not taste anything or put anything into their mouths during the lab.

Rubric and Additional Student data

Table E.1. Number of students with complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N) in the ASA kinetics titration pre-lab questions.

Pre-lab Questions	Points	Initial				Review			
		C&C	C	SC	N	C&C	C	SC	N
Question 2 – rate expressions (symbolizing)	9	78%	19%	4%	0%	93%	7%	0%	0%
Question 7 - coefficients vs. exponents (comprehension)	1	41%	0%	0%	59%	41%	0%	0%	59%
Derive generic rate expression for ASA hydrolysis (matching and symbolizing)	3	52%	30%	15%	4%	85%	11%	4%	0%
Question 1 – enthalpy (retrieval)	5	26%	27%	30%	19%	59%	26%	11%	4%
Determine sign of ΔH (making decisions)	4	74%	26%	0%	0%	85%	15%	0%	0%
Question 4 – calculation diagram (metacognitive skill)	5	19%	30%	48%	4%	63%	19%	19%	0%
Question 5 – calculation table, answers (solving problems)	10	78%	4%	19%	0%	81%	11%	7%	0%
Question 5 – calculations (integrating and comprehension)	12	78%	19%	4%	0%	89%	11%	0%	0%
Stoichiometry (retrieval)	6	100%	0%	0%	0%	100%	0%	0%	0%
Derivation of order and k, coefficients vs. exponents (comprehension and analysis)	9	30%	30%	30%	11%	74%	11%	7%	7%

Table E.1. Number of students with complete and correct responses (continued).

Pre-lab Questions	Points	Initial				Review			
		C&C	C	SC	N	C&C	C	SC	N
Pseudo order and experimentation (knowledge utilization and experimenting)	8	0%	0%	0%	100%	0%	0%	0%	100%
Question 6 – Pictorial diagram (solving problems)	20	37%	30%	22%	11%	63%	22%	11%	4%
Rate vs. time (generalizing and experimenting)	8	26%	44%	19%	11%	52%	37%	0%	11%

Table E.2. Rubric and percentage of FS students with C&C, C, SC and N responses.

Section	Points	Average	C&C	C	SC	N
Procedure	5	91%	82%	10%	8%	0%
Tables	6	97%	95%	3%	0%	3%
Units on the graph	6	92%	90%	0%	8%	3%
Title on the graph	3	69%	64%	5%	5%	26%
Axis of the graph	6	75%	64%	18%	3%	15%
Trend line drawn to the graph	4	66%	62%	8%	3%	28%
Equation of the line	3	65%	64%	3%	0%	33%
R ² / most linear line	4	32%	13%	31%	21%	36%
Determine <i>k</i>	5	59%	56%	0%	3%	41%
Modifications suggested	5	52%	46%	5%	10%	38%
Devise a question and answer	3	56%	18%	46%	23%	13%
Application question: Measurement of one sample at a time	5	61%	44%	10%	26%	21%
Conclusions drawn	10	71%	62%	23%	5%	10%

Table E.3. Percentage of first semester students with C&C, C, SC and N responses (section of lab separated and graded based on correctness).

Section	Average	C&C	C	SC	N
Moles calculation	23%	23%	0%	0%	77%
Concentration calculation	23%	23%	0%	0%	77%
State time	10%	0%	21%	0%	79%
Use of R^2	26%	26%	0%	0%	74%
graph $\ln[asa]$	85%	85%	0%	0%	15%
graph $1/[asa]$	38%	0%	77%	0%	23%
use of graphs	67%	67%	0%	0%	33%

Table E.4. Rubric and Percentage of second semester students with C&C, C, SC and N responses.

Section	Points	average	C&C	C	SC	N
Kinetics graphs provided	3	64%	44%	11%	33%	11%
Trend line	3	43%	37%	4%	7%	52%
Linear regression, R^2	2	59%	48%	22%	0%	30%
Shape and order of graphs	2	54%	48%	11%	0%	41%
Determine k	3	74%	70%	4%	4%	22%
Catalyst energy profile	8	53%	30%	37%	11%	22%
Explanation of pseudo reaction order	3	56%	41%	11%	22%	26%
Conditions necessary to explore reaction (making decisions)	3	65%	56%	7%	15%	22%
Application kinetic graphs and expressions (matching)	6	35%	26%	0%	0%	74%
Units of k (symbolizing)	1	74%	74%	0%	0%	26%
Relationship between graphs and expressions (making decisions)	2	69%	48%	41%	0%	11%
What is meant by pseudo-first order reactions (generalizing)	2	80%	70%	15%	0%	15%
How it is different from first order reactions (integrating)	1	78%	52%	0%	0%	48%
How is it different from second order reactions (integrating)	1	30%	30%	0%	0%	70%
Derive equations and graphs (symbolizing)	20	91%	96%	4%	0%	0%
Terminology and diagram (problem solving)	32	61%	44%	22%	22%	11%
Temperature and collision theory (making decisions)	3	56%	19%	33%	44%	4%
Graph applications (symbolizing)	1	67%	67%	0%	0%	33%

Table E.3. Rubric and Percentage of second semester students responses (continued).

Section	Points	average	C&C	C	SC	N
Trend as it relates to graphs and data (generalizing)	3	39%	15%	19%	37%	30%
Slope of the line (integrating)	6	82%	74%	22%	0%	4%

Post-lab Question: Temperature affects E_{act} and the collisions between molecules. Referring to this statement, state how temperature impacts k and summarize your findings on the effect of temperature rate in this diagram? (C&C response).

Sample response: “When temperature changes with Arrhenius Expansion $k = Ae^{\frac{Ea}{RT}}$, A is not really affected, however, the expression of $e^{\frac{Ea}{RT}}$ changes meaning more molecules are available to react in excess of the Activation Energy. Even a slight increase in temperature makes the expression increases significantly when this $e^{\frac{Ea}{RT}}$ expression increases then so does k at almost the same magnitude. In reviewing the previous diagram, it is noted that the conditions of Scenarios A with a higher temperature cause increased collision of molecules (so reaction becomes faster) and increased k compared with the lowered k values of Scenario B and C when temperature is lowered to 30C. Note that in these scenarios, k was decreased to $.05\text{s}^{-1}$.”

Table E.5. Average and medium scores for SS section for the entire lab grade.

Students	Average	Median	Number of students
Lab grade			
SS – Section 014	86% ± 10%	88%	8
SS – Section 022	79% ± 11%	83%	11
SS – Section 024	84% ± 7%	84%	8
All SS sections	82% ± 10%	85%	27

Additional Experimental Data

The concentration of acetic acid in the air around the set-up was calculated for the quantities of acetylsalicylic acid used. The volume of air around the set-up was estimated at 3.6 L and the volatility calculated as 131600 mL/m³ where the vapor pressure is 100 mm Hg at 63°C. The reaction is assumed to be at 100% efficiency and the volatility is relatively constant between 60-70°C.

Table E.6. Concentration of acetic acid in air around experimental set-up.

Moles	Volume, mL	Volume which is volatile, mL	Concentration, ppm
0.006	0.318	0.042	11.6
0.011	0.636	0.084	23.2
0.017	0.953	0.125	34.8
0.022	1.271	0.167	46.5
0.028	1.589	0.209	58.1

Appendix F. Thermometric Titrations

Thermometric Pre-laboratory activity

Name: _____ Lab section: _____ Lecture table #: _____
T.A.: _____ Group: _____ Date: _____

Part A. You are assigned **one** of the following reactions. Perform the reaction assigned in a test tube and gently shake. Immediately observe by touching the *test tube* and record the temperature of the reaction with the thermistor. All chemicals are assumed to be at room temperature before the reaction. Note the room temperature. Indicate the direction that the heat transfer (hand \rightarrow solution/tube or hand \leftarrow solution/tube) and determine ΔH (positive or negative values i.e. endothermic or exothermic).

Part B. Repeat your reaction in a Styrofoam cup. Observed the temperature of the reaction through the Styrofoam cup and using a thermometer.

Complete tables for Part A and B and obtain the data for the *other* reactions from other groups *before* leaving the lab.

Caution: Be careful with all chemicals. Acids and bases are corrosive.

1. $\text{KOH}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{KOH}_{(aq)}$ - Dissolve ~0.5g KOH in 5mL of water.
2. $\text{H}_2\text{SO}_{4(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{4(aq)}$ - Dilute 5mL of H_2SO_4 in 2mL of water (add acid to water).
3. $\text{NH}_4\text{Cl}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{NH}_4\text{Cl}_{(aq)}$ - Dissolve ~0.5g NH_4Cl in 5mL of water.

Part A: Test tubes

Room temperature:

Reaction	Observation		Direction of heat flow (to/from solution)	Temperature, °C	ΔH (+/-)
	Touch	See			
1					
2					
3					

Part B: Styrofoam cup

Reaction	Observation	Temperature, °C	ΔH (+/-)	Direction of heat flow (to/from solution/ none)
	Touch (as compared to Part A)			
1				
2				
3				

Questions (answer on the back of this page):

- i) Depict microscopically the chemicals before and after the reaction for the assigned reaction.
- ii) Explain briefly how the flow of heat allows you to observe the enthalpy and temperature changes in these reactions.
- iii) Based on your observation, explain why hot coffee is usually put in Styrofoam cups rather than glasses.

Time limit 10 minutes – work efficiently. Hand in this completed sheet with the Post-lab questions.

TA signature: _____

Thermometric Titration and ΔH_n Pre-lab

Experimental procedure:

You will not be allowed to use the experimental procedure handout in the lab. Your experimental procedure must be checked by your instructor before you can perform the experiment. Your pre-lab procedure should concisely include:

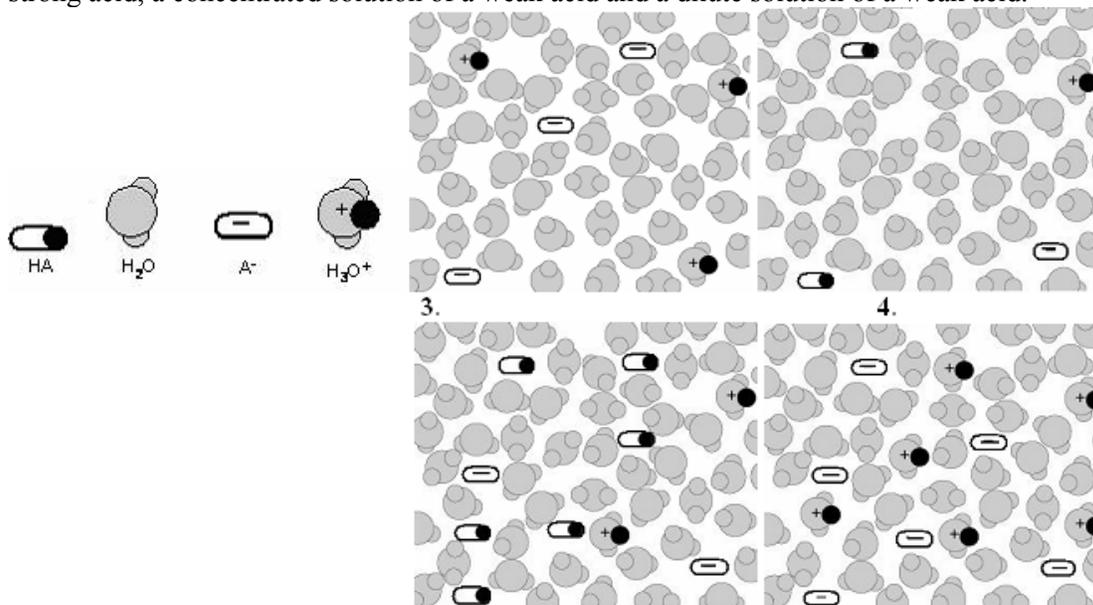
1. Briefly **outline** your experimental and learning objectives. What is the question you will be answering or exploring in the lab? What do you expect to learn from this experiment?
2. **Describe** the experimental procedure in your *own* words. You may use any method you like such as bullet points or diagrams. Be brief, but clear as this will be the procedure you will use to perform the experiment.
3. Briefly **describe** the operation of the buret and pipet. Cite any source your use.
4. What is meant by the terms: conditioning, standard solution and standardization?
5. What do you expect the outcome of your experiment will be?

Name: _____ Lab section: _____ Lecture table #: _____
 T.A.: _____ Group: _____ Date: _____

Thermometric Titration and ΔH_n Pre-laboratory Questions (Revised)

Note: These pre-lab questions **must** be completed before the lab and turned to the instructor on the date announced. **Read the entire experiment before answering these questions!** Review the topics: enthalpy, calorimetry, and acids and bases.

1. The diagrams below represent: a concentrated solution of a strong acid, a dilute solution of a strong acid, a concentrated solution of a weak acid and a dilute solution of a weak acid.¹

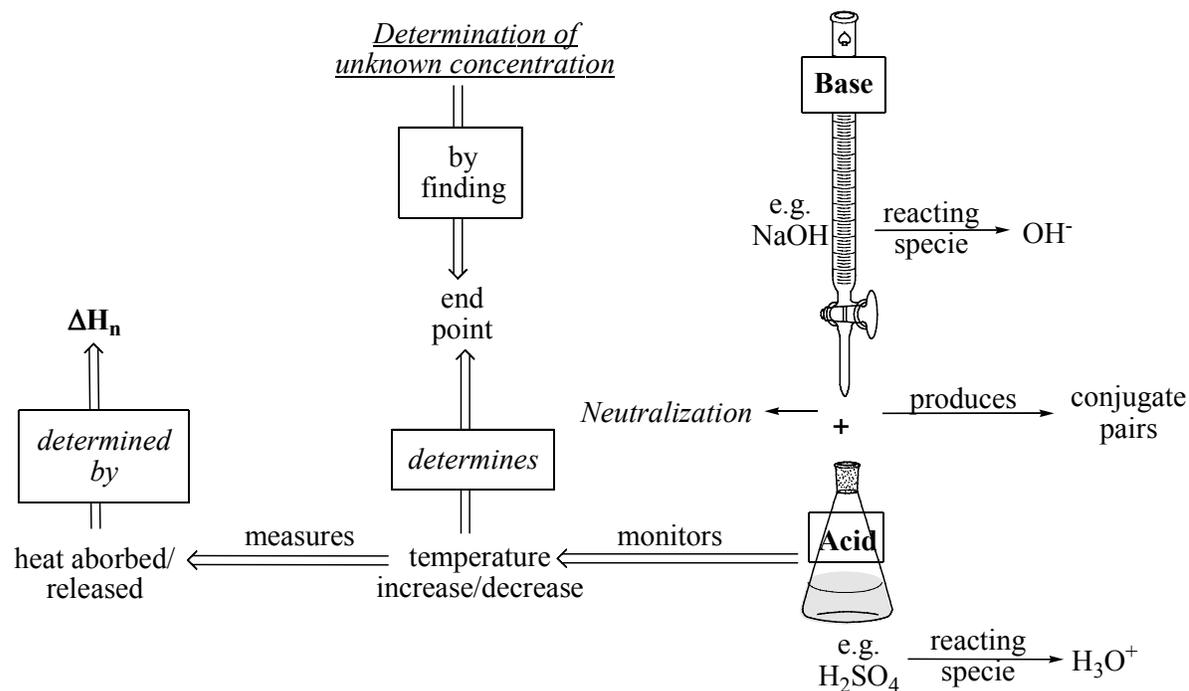


Indicate by the diagram number in the table below which diagram represents each of the four solutions. Briefly explain your answer giving an example of a strong and weak acid.

(¹Diagram adapted from Taber, K. S. Chemical misconceptions - prevention, diagnosis and cure, L: Volume 2: classroom resources, London: Royal Society of Chemistry, 2002.)

Acid	Strong: e.g. _____	Weak: e.g. _____
Concentrated	# ____ Explain:	# ____ Explain:
Dilute	# ____ Explain:	# ____ Explain:

2. With reference to the diagram below answer the following questions. You may add any information to the diagram that may assist you in answering the questions.



a) Briefly explain how ΔH_n can be used to determine the H_3O^+ concentration in a neutralization reaction.

c) Give the resulting conjugate acid-base pairs.

Acid and conjugate base: _____

Base and conjugate acid: _____

3. You may use the conversion diagram and sample calculation table in Figure 1 below to answer the following questions. You may add to the diagram or develop your own calculation method, however all work *must be shown*.

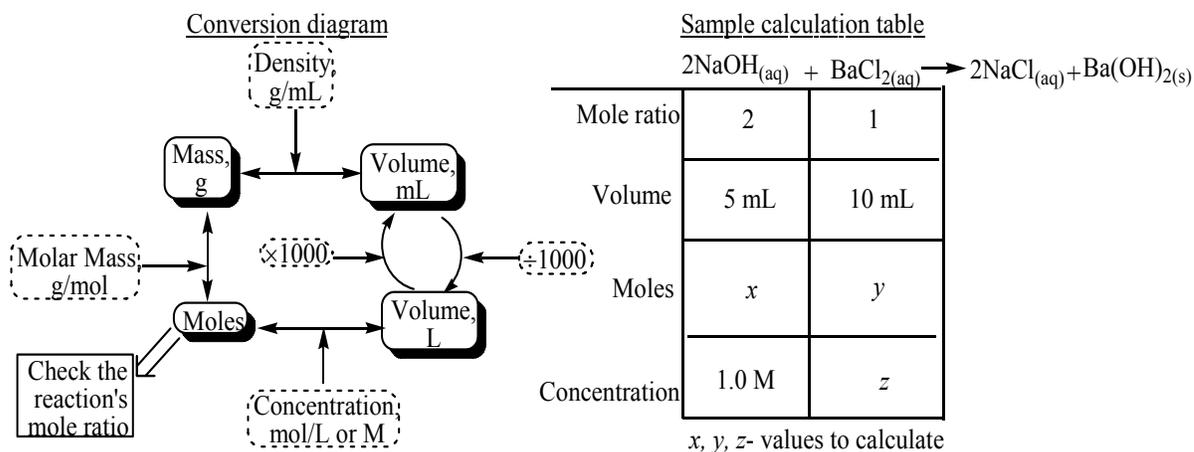
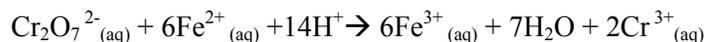
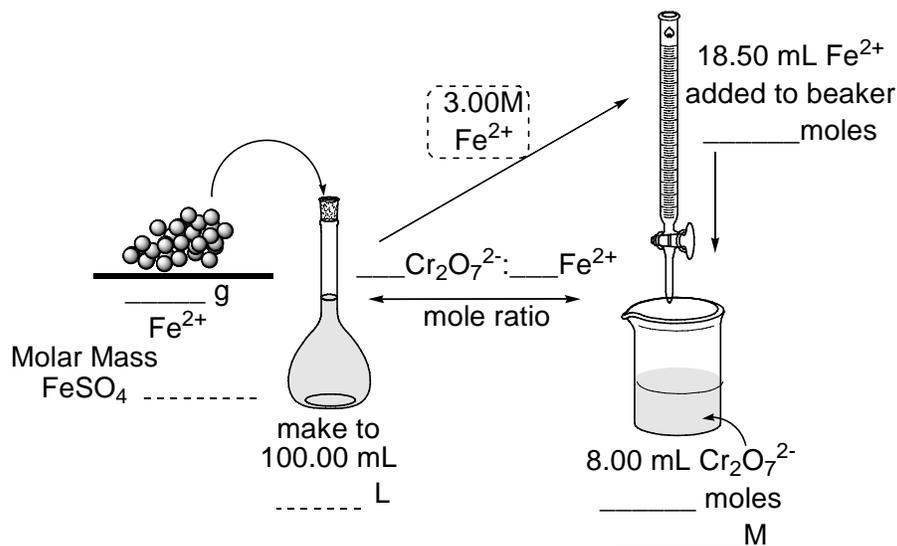


Figure 1. Conversion diagram and sample calculation table.

4. You make a 3.0 M solution of iron II sulfate. You determine the concentration of potassium dichromate that completely oxidizes the iron II sulfate solution using the reaction as shown below.



a) Complete the diagram below to determine the concentration of dichromate and show all calculations



b) You observe a 5°C increase from the start of the titration to the end point resulting in an initial slope of 0.3 °C/L. Represent this information as a graph (ΔT , °C vs. Volume, L) and calculate ΔH_r where $c_f=20 \text{ J/}^\circ\text{C}$.

Graphs (give details)

Calculations (Show all)

Is the reaction exothermic or endothermic?

5. You determine the concentration of NH_4Cl by performing a thermometric titration using 0.5 M KOH solution. You require 10.00 mL of the base to reach the end point to neutralize 5.0 mL of the acid. A 2°C change is observed resulting in an initial slope of -0.2°C/L and ΔH_r for the reaction is 25 J/mol.

a) Write a balanced equation for the reaction. Indicate the conjugate acid and base. Is the conjugate base weak or strong? Explain briefly reference to pre-lab question 1.

b) Draw a diagram like question 2 depicting the thermometric titration data given. Calculate the concentration of NH_4Cl and c_t . Is the reaction exothermic or endothermic? *Show all calculations!*

Thermometric Titrations and ΔH_n Determination Experiment

Introduction: Titration is an analytical method used to determine the unknown concentration of an analyte from the known concentration of a titrant. The titrant is added to the analyte until a stoichiometric volume has been added to obtain the end point. The concentration of the analyte is determined from the known concentration and volume of the titrant at the end point. Data of temperature vs. volume is obtained in a thermometric titration and is used to determine the end point of acid-base and redox titrations by utilizing the enthalpy change of reaction (ΔH , heat given off or absorbed, concept explored in the pre-lab activity). The addition of titrant induces temperature changes as a consequence of the *enthalpy change* associated with the reaction and the resulting graph is relatively linear *until* the end point, after which addition of excess titrant will create an *inflection point*. This inflection point allows for easy identification of the end point. The end point can therefore be *extrapolated* from the titration graph of temperature (T , $^{\circ}\text{C}$) vs. volume of titrant (V_t , mL).

$$\Delta T = -\Delta H_n(M_t V_t / c_t) \quad \text{Equation 1}$$

$$d\Delta T / dV_t = -\Delta H_n(M_t / c_t) \quad \text{Equation 2}$$

$$d\Delta T = \underbrace{-\Delta H_n(M_t / c_t)}_{m\text{- slope}} dV_t + 0 \quad \text{Equation 3}$$

↙ intercept

$$\therefore \Delta H_n = -mc_t / M_t \quad \text{Equation 4}$$

Notes:
 c_t – total heat capacity, $\text{J}/^{\circ}\text{C}$
 ΔT – temperature change $T_f - T_i$
 (analyte), $^{\circ}\text{C}$
 M_t – molarity of titrant, M
 V_t – volume of titrant, L
 $d\Delta T / dV_t$ – differentiated equation gives slope (m)

ΔH_n (enthalpy of neutralization, J/mol) is the enthalpy change generated from the reaction of *equal moles of acid and base* and can be obtained via Equation 1. Since the thermometric titration measures the enthalpy change at equal moles of the acid and base, ΔH_n can be calculated from the data. ΔT is obtained by finding the difference in temperature after each addition of titrant from the *initial temperature* (analyte) (equation 5). The graph of change in temperature (ΔT , $^{\circ}\text{C}$) vs. volume of titrant (V_t , L) can be used to obtain ΔH_n by the differential Equation 2. ΔH_n can therefore be determined from the initial slope, $d\Delta T / dV_t$, of the ΔT vs. V_t graph (Equation 3-4).

$$\Delta T = T_f - T_i \quad \text{Equation 5}$$

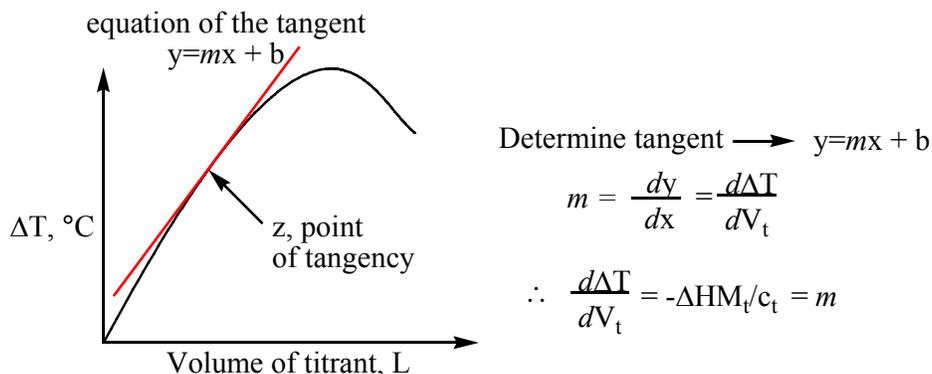
T_i – temperature of analyte (L of titrant)
 T_f – temperature at each volume of titrant

There are different methods for determining the initial slope of the curve: tangent to or derivation of the curve. Both methods are explained briefly below. Please note that you will be assigned one of the two following methods to determine slope of the curve, so consult any Math text for help.

Method A: Tangent to curve (Mathematical Approach)

A tangent line (line which touches one point on the curve only) is drawn (Graph 1). Since the tangent line must only touch one point on the curve. Any suitable method can be used to draw the best tangent line, such as drawing secant lines in Excel or using a ruler to draw a line of tangency to the curve. The slope of this line is determined by calculation (dy/dx) or adding a trend line in Excel to obtain the equation of the line.

Method A

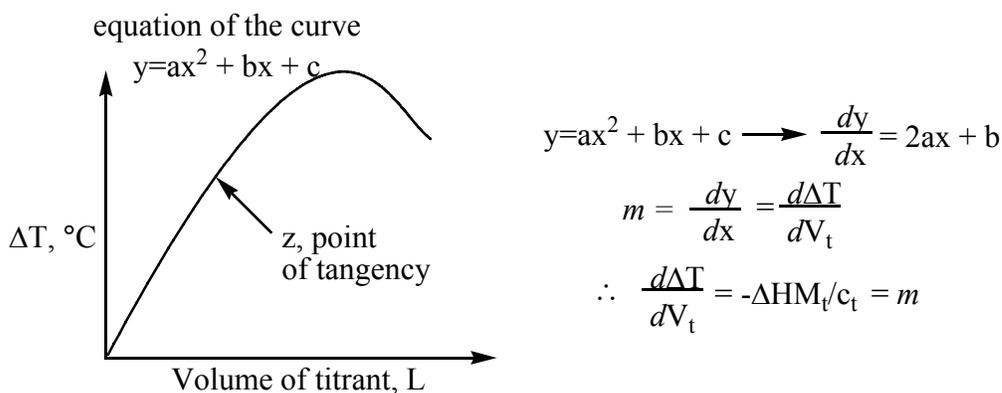


Graph 1. Determination of ΔH_n using Method A.

Method B: Alternative trend line method (Excel-Calculus Method)

A polynomial trend line can be added using Excel and the equation of the curve obtained (Graph 2). The derivation of the polynomial equation (dy/dx) allows for the calculation of the slope of the line at point z, just as in Method A. The x coordinate for the point of tangency is used in the derived equation to obtain the slope.

Method B



Graph 2. Determination of ΔH_n using Method B.

Experimental inquiry: Utilize thermometric titrations to monitor the progress of acid-base and redox titrations to determine end points in order to calculate the unknown concentrations of the analytes. Acid-base titration data collected is used for the determination of ΔH_n in order to draw conclusions about the nature of the reaction.

Safety: Acids and bases are corrosive and may cause burn. Potassium permanganate may be flammable, causes *stains* and could cause burns. Consult the instructor about chemical spills and burns. Practice how to use the buret and pipet with water if you have never used them before. The TA can demonstrate proper techniques.

Procedure:

Part A. Determination of the end point of a thermometric titration of 1.0 M NaOH (standard solution) vs. ~ 1 M HCl.

1. Clean and thoroughly dry all glassware and Styrofoam cups.
2. Condition the pipette with a small amount of HCl (~ 1.0 M) and the buret with 1.0 M NaOH. Before beginning, record the exact concentration sodium hydroxide written on the reagent bottle in the data table and use this value for future calculations. *NaOH is the titrant!*
3. Place one Styrofoam cup inside the other; place a stir bar inside the inner cup. The use of the Styrofoam cup over glassware was explored in the pre-lab activity. Pipet exactly 10.0 mL of HCl into the Styrofoam cup. Place the cups on the stir plate and cover with the given cap as shown in Figure 1.

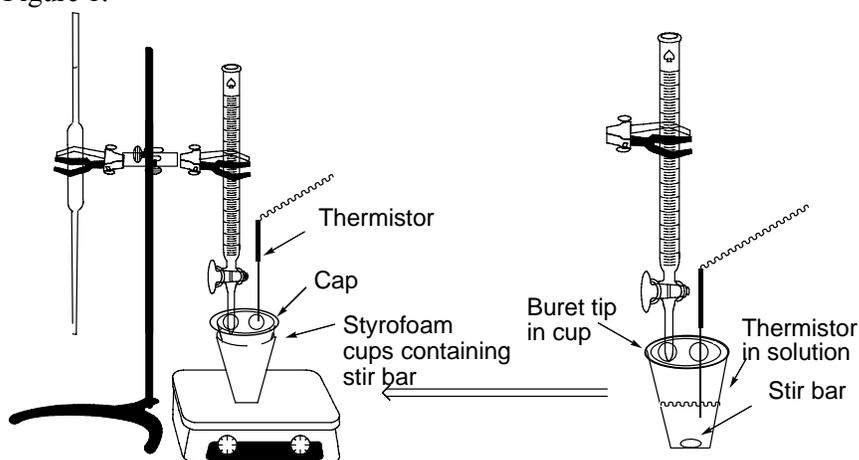


Figure 1. Thermometric Titration apparatus set-up.

4. Fill the buret with 1.0 M NaOH and allow the tip of the buret to be filled by opening the stopcock, and releasing some NaOH in a *waste* container. Place the buret in the clamp, positioning the buret so that the only the tip goes through the one of the holes in the cap as shown in Figure 3.16. Position the thermistor using a clamp in the solution through the opposite hole in the cap, but do not allow the thermistor to touch the cup or stir bar.
5. Begin the first titration by adding 1 mL increments of NaOH and recording the stable temperature *10 seconds* after each addition. Make the next addition is *before 30 seconds of the last*. **Note:** If the thermistor does not have a chance to stabilize or the time between additions is too long allowing the temperature to drop, the data will be imprecise for the remainder of the titration.
6. Present the data in a table similar to Table 1 (additional rows will be needed).

Table 1. Data table for the titration of the analyte vs. titrant in Part X.

Trial 1		Trial 2		Trial 3	
Volume, mL	Temperature, °C	Volume, mL	Temperature, °C	Volume, mL	Temperature, °C
Use the two closest extrapolated values from the graphs for the average: End point 1: _____ mL Acid End point 2: _____ mL Acid Average of 1 & 2: _____ mL Acid Concentration of NaOH: _____ M					TA Signature _____

7. Add a total of 15.0 mL NaOH to the reaction. *Observe the inflection point!* Report the data in a table as shown in the Results section.

Note: If the highest temperature remains constant for a range, use the last volume value at this temperature.

8. Repeat the titration in the same manner as above; however, to find a more accurate end point, perform the titration in smaller increments ($\sim 0.10\text{-}0.50\text{ mL}$) at a 1 mL range before and after the inflection point (between $\sim 9\text{-}11$ mL for HCl only). You are still required to add each addition *within* 30 seconds of each other.

Note: Larger increments may be added, such as 2 mL, before the 1 mL range before and after the inflection point. The purpose of adding these points is to obtain points on the curve in order to *extrapolate* the end point from the graph. Refer to the introduction.

9. Once an end point has been narrowed down, repeat the titration to obtain accuracy of the value. Work carefully, as the analysis needs to be within a 1% agreement.

10. The *approximate* concentration of HCl was given as guidance to practice this technique. Obtain the exact HCl concentration from your instructor in order to determine the percent error of the data.

Part B: Determination of the end point of a thermometric titration of 1.0 M NaOH vs. HNO₃.

Repeat the same procedure as Part A, using HNO₃ instead of HCl. However an approximate HNO₃ molarity is not given as guidance, so more care is needed in this titration. To find the inflection point (step 7) and extrapolate the endpoint, add ~ 5 mL excess NaOH *after* observing a change in the linearity of the temperature data.

Part C: Redox thermometric titration using known concentration of potassium permanganate to determine the concentration of ferrous ammonium sulfate hexahydrate (Fe²⁺) in acid.

Repeat the same procedure using a known concentration of KMnO₄ as the titrant and measuring 10.0 mL of Fe(NH₄)₂(SO₄)₂·6H₂O (acidified) into the Styrofoam cups as in Part B.

Part D: Clean-up

Wipe up any chemical spills. Dispose of chemicals in the corresponding waste containers. Rinse glassware with water and iron cleaning solution to remove any stains from Part C.

Post-Lab Report

Type or legibly write the titration results and responses to discussion questions. Answer the general questions in the spaces provided (write legibly). Graphs *must* be drawn with MS excel and diagrams may be drawn neatly by hand or using an art program. Tangents and extrapolations may be neatly hand drawn or drawn in excel.

Results and Discussion

1. Write balanced equations for the reactions in Parts A-C using correct symbols for the states of matter. Consult the Standard Reduction Tables for help with the equation in Part C.
2. Present the data for Parts A-C in tables as shown in Table 1. Label each table appropriately, to describe the titration performed.
3. Plot graphs of temperature, °C (y-axis) vs. volume of titrant, ml (x-axis) for the two more accurate titrations in Parts A-C. Ensure each graph *fills the entire plot area*, occupies no less than half of a page, and has correct labels and titles. Extrapolate and identify the end point clearly on each graph.
4. Before leaving, all tables and graphs must be completed and signed by the TA. Return *all* data with the post-lab report, including those with signatures.
5. Determine the average end point of each titration using the *closest 2 extrapolated values*, indicating this in the tables. Calculate the unknown concentrations of the acids and the oxidizing agent. You may use tables or diagrams to aid your calculations as done in the pre-lab questions, but *show all work*.
6. Calculate the percent error for the HCl concentration based on the data and the actual concentration given after the titration.
7. Use the titration data to plot *graphs of change in temperature, °C vs. volume, L* for the best two titrations in Part A. Use appropriate titles and labels for each graph. Use these graphs to calculate the ΔH_n by the method (A or B) assigned by the instructor and determine the average ΔH_n . $c_t = 83.6 \text{ J/}^\circ\text{C}$ for this titration. Show all work.
8. Give a reason why the graph of ΔT vs. V_t above is plot in *units* of L rather than mL as done with the previous graphs? If volume was plot in units of mL, does this affect the calculated ΔH_n value?

Conclusion

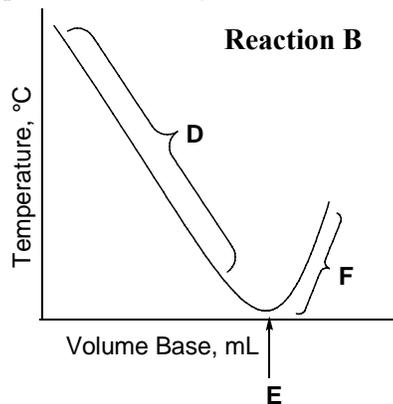
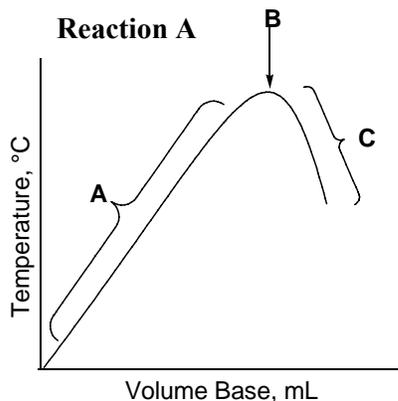
1. Were the reactions observed in this thermometric titration lab exothermic or endothermic? Briefly, justify the answer with experimental and calculation evidence.

2. Identify at least experimental 3 errors, excluding not following directions or incorrectly measuring volumes. What can be done to account for the errors you have noted in answer?
3. What other factors influence the evolution of heat in the acid-base reactions; give at least 2 reasons? *Consider the pre-lab activity.* How could you account for the factors you gave in answer?
4. Consider the experiment and the colorimetric titration demonstration by the TA, what are the advantages and disadvantages of titration and in what circumstances would you use each?
5. Give a practical application of titrations in the real world (be specific).
6. Re-examine your pre-lab answers. Have any of your original thoughts changed or been clarified? Make corrects to the pre-lab and submit the corrected pre-lab with a brief justification your changes.
7. Devise a plausible and thoughtful question related to this experiment (it should be sufficiently different from the questions given). This question may be chosen for discussion.

Thermometric Titration Post-Lab Questions

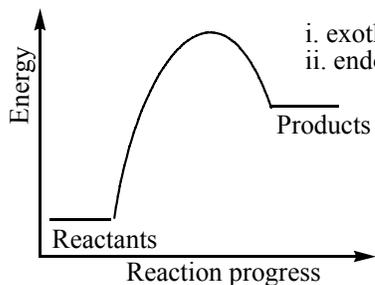
Name: _____ Lab section: _____ Lecture table #: _____
 T.A.: _____ Group: _____ Date: _____

1. a) The graphs below represent two different acid-base thermometric titrations. Indicate what is occurring in the reaction flask at the parts labeled A-F in terms of the acid and base reacted, temperature and energy changes with respect to heat being released or absorbed during the titrations.



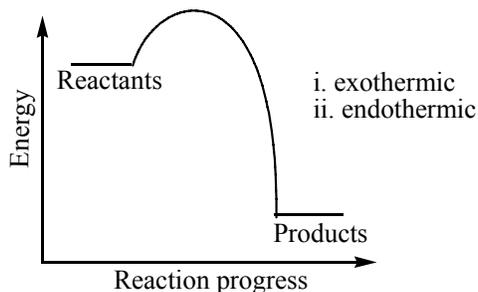
	Acid and base reacted	Temperature changes	Energy/heat changes
A			
B			
C			
D			
E			
F			

b) What is the enthalpy change (exothermic and endothermic) of the titrations depicted above and which energy profile diagrams represents each reaction. Rationalize using an example from the pre-lab activity.



Reaction: A or B

Reason:



Reaction: A or B

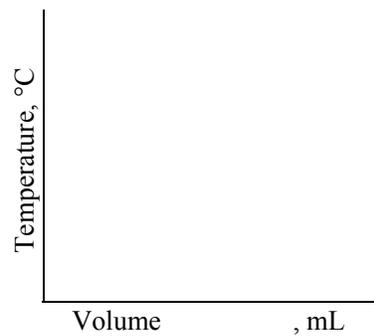
Reason:

Example reaction from the pre-lab activity:

Example reaction from the pre-lab activity:

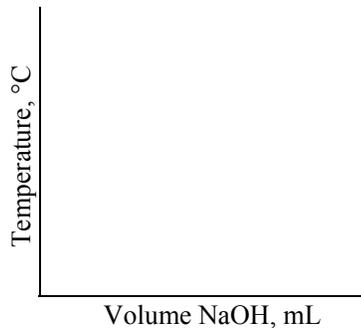
2. a) What would happen to the temperature if 1mL portions of HCl solution had been added to NaOH, instead of the way the experiment was performed? Sketch the expected graphs.

Observation

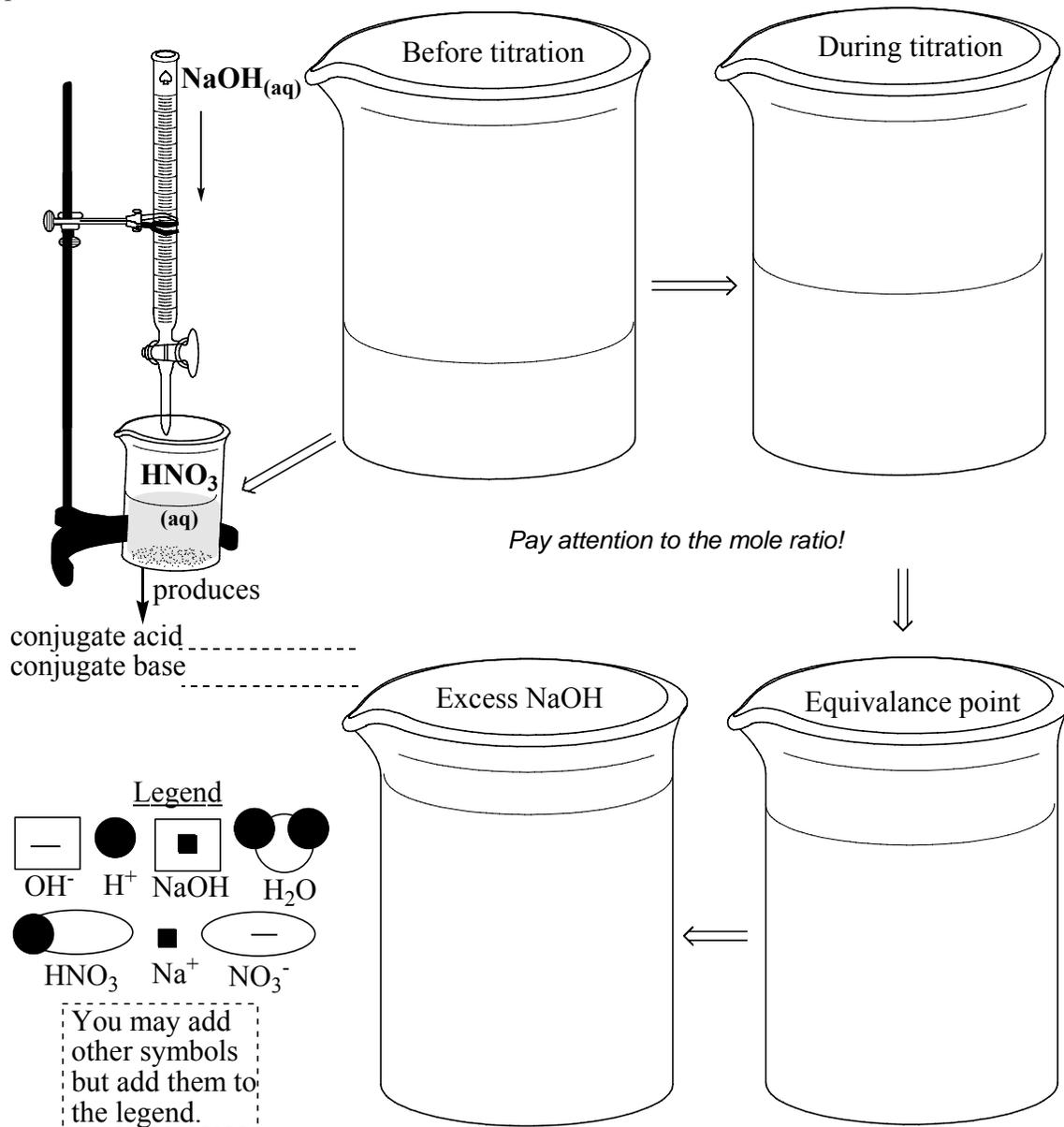


b) Draw the expected curve for a diprotic acid (2 ionizable protons)? Briefly, rationalize the shape of the graph.

Explanation

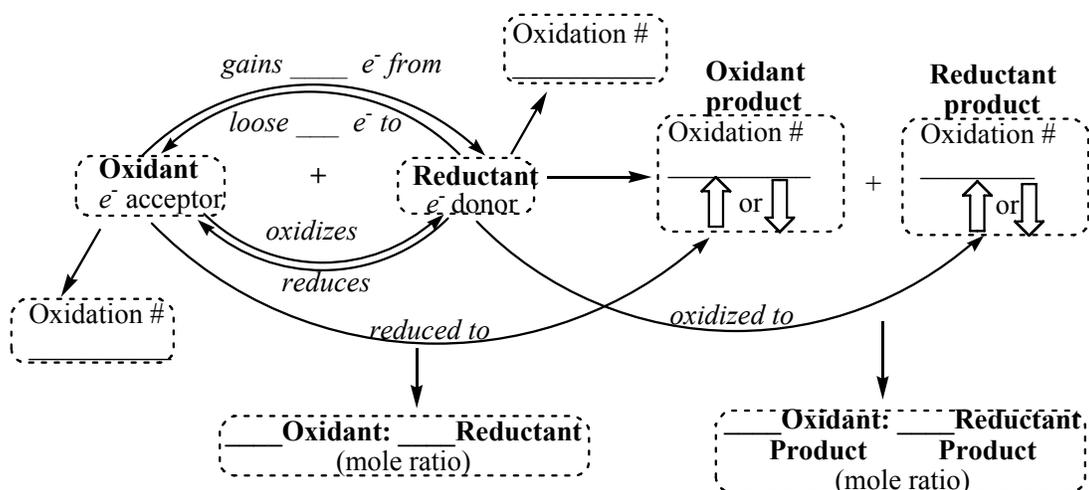


3. a) Complete the diagram below to depict the interaction of the reacting species in Part B that led to neutralization. Referring to the diagram, explain why the highest temperature is used as the end point.



Explanation:

b) Is the resulting conjugate acid strong or weak? Why? Explain with reference to pre-lab question 1.



Oxidant

Oxidant product

4. **Reductant**

Reductant product

a) i) Using the reaction in Part C, replace the bolded words in the diagram above with the reactants and products in the experiment by filling in the blanks below the diagram.

ii) Calculate and fill in the oxidation numbers of the reactants and products in the diagram.

Calculations:

iii) Circle the arrows indicating if the oxidation number increased or decreased.

iv) Give the stoichiometric ratios between the reactants and the ratio between the products.

b) Write half-reactions and full *ionic* equations based on the answer in (a) (balance the equation and include states of matter). Consult the Standard Reduction Tables.

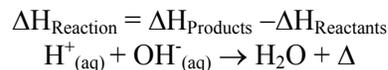
Half reactions:

Full ionic equation:

Thermometric Titration Instructor's Notes

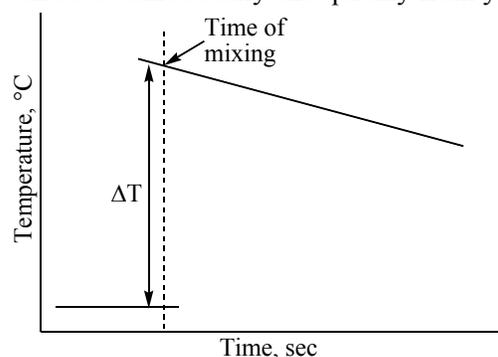
Purpose: In this experiment, students will be exploiting the heat of neutralization of an acid base reaction and the heat of a redox reaction to determine the endpoints of these types of titrations. A thermometric titration is an adiabatic system producing a plot of temperature versus volume of titrant to determine an end point. The endpoint will be marked by the highest reading on the thermometer or probe during the course of the titration. This experiment can easily be adapted for students who are color-blind or visually disabled using a talking thermometer.

Heat of neutralization is the heat evolved when an equivalent of acid reacts with an equivalent of base.



The neutralization of strong mineral acids is exothermic and the changes in temperature as more base is being added can be easily monitored. The production of heat in the reaction will increase until the reaction is neutralized. At the point that the reaction is complete, the highest temperature is achieved, and this is noted as the endpoint. The temperature will then drop as more base is added to a cooler solution is being added to a warmer solution at a point when no more heat is being generated. A similar observation is seen for the redox reaction.

Heat of neutralization (or enthalpy of neutralization, ΔH_n , J/mol) is the heat generated from the reaction of an acid and a base. Traditional undergraduate experiments to determine heat of neutralization use the Styrofoam cups to produce a graph of temperature vs. time (Graph 3.7), where the difference between the initial and final temperatures is obtained, ΔT . This value of ΔT is used to calculate q (Equation 1) which is then used to determine ΔH_n (Equation 2). However, ΔH_n can be obtained easily and quickly from your thermometric titration.



Graph 3.7. Enthalpimetric graph for the determination of ΔH_n .

$$q = mc\Delta T = c_t \Delta T$$

$$q = -\Delta H_n (n_p)$$

$$\therefore \Delta T = -\Delta H_n (n_p) / c_t = -\Delta H_n (M_t V_t / c_t)$$

$$d\Delta T / dV_t = -\Delta H_n (M_t / c_t)$$

$$d\Delta T = \underbrace{-\Delta H_n (M_t / c_t)}_{m\text{- slope}} dV_t + \underbrace{0}_{\text{intercept}}$$

$$\therefore \Delta H_n = -mc_t / M_t$$

Equation 1

Equation 2

Equation 3

Equation 4

Equation 5

Equation 6

c – specific heat capacity, $J/g^{\circ}C$
 c_t – Total heat capacity, J/K or $J/^{\circ}C$,
 $c_t = c_s m_w$
 q – amount of heat, J
 n_p – moles of product, $n_p = M_t V_t$
 ΔT – change in temperature $T_f - T_i$, K or $^{\circ}C$
 m – mass, g
 M_t – molarity of titrant, M
 V_t – volume of titrant, L
 $d\Delta T / dV_t$ – differentiated equation gives slope (m)
 T – temperature, K or $^{\circ}C$
 m – slope of the line

The thermometric titration experiment is used to determine the endpoint of acid-base and redox titrations (temperature vs. volume, first part of the experiment), but can be extended include calculation of ΔH_n . This thermometric method allows for an estimation of heat of neutralization by graphing ΔT vs. volume under various conditions/assumptions discussed below. ΔT is obtained from the initial graph of temperature vs. volume by calculating the ΔT values (temperature after each addition of the analyte minus initial temperature of the titrant). Heats of neutralization can be determined from the initial slope, $d\Delta T / dV$, of the thermometric titration curve (Equations 3-6).

Note: A polynomial trend-line is a curved line that is used when data fluctuates/curves (3). Proceeding with the titration more than ~ 5 mL past the endpoint will lead to errors in calculation using the calculus approach. This may be remedied, but omitting those data points that are 5 mL past the endpoint or result in a constant temperature for a prolonged addition (curve tail).

Reagents used (CAS numbers)

Nitric acid - 7697-37-2

Hydrochloric acid - 7647-01-0

Sodium hydroxide - 1310-73-2

Potassium permanganate - 7722-64-7

Ferrous ammonium sulfate hexahydrate – 7783-85-9

Sulfuric acid - 7664-93-9

Preparation of reagents:

The desired concentrated solutions are made according to the following table and placed in 1000 mL volumetric flasks. Estimate about 50 mL of each acid and about 100 mL of sodium hydroxide for each group.

Preparation for 1L solutions:

~1M HCl Solution: ~ 500 mL of D.I. water was added to a volumetric flask followed by the acid, the remaining water was added to fill the flask to the mark and the flask swirled carefully. The acid in a glass bottle and labeled with the concentration.

1.0M Sodium Hydroxide: The NaOH is weighed into a weighing dish and immediately transferred into the flask. The flask is filled to 1000 mL mark with deionized water and capped. The flask is shaken vigorously to ensure complete mixing. The sodium hydroxide may be placed in a plastic bottle.

0.007M Potassium Permanganate: KMnO_4 is weighed into a weighing dish carefully and then added to the flask. The flask is filled with D.I. water and the solution is stirred or shaken for a period of time as it takes a while for the solid to dissolve. Once the solid has dissolved, the solution must be placed in an amber or dark bottle away from light in a cool place.

0.003M Ferrous ammonium sulfate hexahydrate: $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ weighed and added to the flask. D.I. water is added to fill the volumetric flask about half filled. The flask is swirled to allow some of the iron to dissolve. The sulfuric acid is then added slowly to the solution, and the remaining water is added to the mark on the flask. The flask is swirl until the solid is dissolved and then the solution is transferred to an amber bottle. All solutions must be kept at room temperature overnight, to allow them to equilibrate before use.

Table F.1. Concentrations and quantity of titration solutions needed.

Concentration of Acid Needed	Amount for 1.00L solution
~1 M Hydrochloric Acid (~12.1N)	82.64 mL
~1.5M HNO_3	94.94mL
1.0 M NaOH (from pellets)	40.00 g
0.07M Potassium Permanganate	11.063g
0.03M Ferrous ammonium sulfate hexahydrate	12.768g (add 27.8 mL 18N H_2SO_4)

Hazards:

The use of strong acids may cause skin burns. It is advised that these acidic solutions be prepared cautiously in the hood. Bases are corrosive and may cause burns. Sodium hydroxide absorbs moisture from the air, so caution should be taken not to leave the pellets or solution open to the air. Potassium permanganate is an oxidant and may cause fires when in contact with strong oxidants. Ferrous ammonium sulfate hexahydrate may be irritating on exposure to the skin and inhalation. General laboratory precautions need to be taken when preparing and handing the chemicals in the laboratory. Students should wear standard laboratory gear such as goggles, closed-toed shoes, and clothing that covers the torso and legs.

Suggestions and Notes:

1. Preparation:

- Make sure all solutions are allowed to achieve room temperature overnight before use.
- Standardize the solutions (NaOH and KMnO_4) prior to using in the experiment to ensure accuracy.
- A cover should be used if the students are able to see the color changes of the permanganate. It can be regular Styrofoam cup caps or plastic weight boats. They must have two holes in them: one for the buret and one for the thermometer. The cap also helps hold the thermometer and buret in placed for the titration if place correctly.
- We found that thermal changes corresponded to the color changes with phenolphthalein, methyl red, and the universal indicator. In many cases, the thermal titration corresponded better as pH of 7 was achieved (a drop or two before some indicators could detect as they have a range in the basic range).

2. In the laboratory and data analysis:

- Various concentrations of hydrochloric acid can be used, but it is advisable to give the students a base-line to look for. Do not give them the exact concentration, but a range within the endpoint.

- Observe the values of the students, and encourage them to repeat the titrations if they are not on the right track. The big source of error is time taken for the students to read the thermometer. Students needed, however, to be reminded that the volume used to determine ΔH_n must be in liters (x-axis) and the y-axis is the change in temperature.

3. *Modifications:*

- This experiment can be used along-side a regular organic indicator such as phenolphthalein and results can be compared.
- If the Styrofoam cups are big enough, beakers or flasks may be used inside the Styrofoam cups.
- For greater accuracy Dewars may also be used.
- Flasks with a side arm in which a thermometer may be inserted and one-hole stopper placed in the top may be used, and fitted inside a Styrofoam cup or into a block of Styrofoam. The buret may be placed inside the one-hole stopper.
- Other acids and bases may be used in the acid-base titration. If diprotic or triprotic acids are to be used in an acid-base titration, students may observe multiple peaks in the graph associated with the removal of each proton.
- A talking thermometer or talking computer probes may be used for students who can not read a thermometer. Students with various visual disabilities may use thermometers with various size numbers. Graphs may also be computer generated automatically depending on the equipment available and traced for the students using raised materials enabling them to find the peaks in their graphs.

4. *Cautions and disposal:*

- If the cups become stained by the permanganate, students may use a small amount of diluted iron solution to remove the stains.
- Have waste bottles available for the redox titration waste.

Post lab:

Students must have a short, but reasonable procedure in their own words. What modifications could *you* have made to the experiment or titrations? Potential answers can be using a purchased calorimeter, using another cup, etc... only accept something reasonable or creative. What modifications would you make or suggestions to improve the efficiency of your titration, even if they are not feasible for a laboratory setting... must be different than above... the first question is related to them, what they did or could have done, this is asking about any reasonable changes at all even if outside their control

Results & Discussion

Students must have tables for each titration with labels and show all your results. Students must draw graphs for each experiment with correct labels for each titration, identifying the endpoints clearly using software e.g. MS excel (no hand written graphs). They must determine their average endpoint (using your closest values) and calculate their unknown concentrations of acid and oxidizing agent (showing all your work). They must describe what they have learnt about titrations, acid-base and redox reactions from this experiment – but not give a generic explanation or definitions.

The student endpoint data were almost identical to that of the instructor in both the stepwise and narrowed down additions. The graphs of the instructor tended to be smoother. The student data

were best after the student was allowed to do a step-wise titration to find a range where the endpoint lies. Student data was also improved after a practice titration (such as that in Procedure A) was performed before a completely unknown acid was titrated. Teacher titrations were run along-side the typical color-changing organic indicators for comparison in order to validate the thermal titration method was accurate. In the acid base-titrations, the thermal titrations were found to be right before the visual endpoint, and closer to the pH of 7 (neutralization point) as expected.

FS Questions and Some Possible Answers to the Pre- and Post-Lab Questions

Pre-lab:

1. Review the following links: <http://www.dartmouth.edu/~chemlab/techniques/buret.html> <http://www.dartmouth.edu/~chemlab/techniques/titration.html>. Describe in your own words the titration procedure, and why it is used.

Answer: Titration is a common laboratory method of chemical analysis which can be used to determine the concentration of an unknown reagent (basically any explanation of how the titration is done). Typically, the buret and pipet are conditioned with the solutions that will be used in it. The initial reading on the buret is done, and the pipet is used to measure out an exact amount of the other solution into the flask/cup. The analyte (known) is added until the endpoint of the titration is obtained (indicator, thermometric, etc). The concentration of the unknown is obtained from the amount of known solution added.

2. What is meant by the term standardization? What is a standard solution and why is it important to use this solution when performing a titration?

Answer: Method by which an analytical reagent's concentration is precisely determined or simply finding the exact concentration of an unknown solution from solution with known concentration. Standard solution is one in which the solution's exact concentration is known (either using a pure substance to begin with or concentration obtained through a titration with a known solution).

3. Define heat of reaction and heat of neutralization? How is this used in today's experiment?

Answer: Heat of the reaction is the heat absorbed or released in a reaction. Heat of neutralization is the heat evolved when one mole of acid reacts with one mole of base. This is applied to determine the endpoint of your titration by looking at the highest temperature (which occurs at the point of neutralization).

4. Write balanced equations for the acid-base reactions of HCl with NaOH (include states). What is the conjugate base and is it strong?

Answer: $\text{HCl}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{NaCl}_{(aq)} + \text{H}_2\text{O}_{(l)}$ [$\text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)}$]
NaCl_(aq) is the conjugate base and it is very weak, because you start with a strong acid and base.

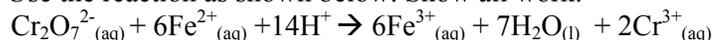
5. Write balanced equations for the acidified redox reactions of permanganate and iron II (to form iron III). Include states and determine your reducing agent.

Answer: $5\text{Fe}^{2+}_{(aq)} + 8\text{H}^+_{(aq)} + \text{MnO}_4^-_{(aq)} \rightarrow \text{Mn}^{2+}_{(aq)} + 5\text{Fe}^{3+}_{(aq)} + 4\text{H}_2\text{O}_{(l)}$; Fe²⁺ is the reducing agent

6. What is the concentration of $\text{Ca}(\text{OH})_2$ if 15.50mL is used to completely neutralize by 10.0mL of 2.00M HCl? Show all work.

Answer: 1 moles of OH, $\text{Ca}(\text{OH})_2 = 2\text{moles of H used, HCl}$; $0.0100\text{L} \times 2.00\text{M} = 0.020\text{moles HCl}$, therefore $0.010\text{moles Ca}(\text{OH})_2$ used $(0.020\text{moles}/2)$. $0.010\text{moles}/0.0155\text{L} = 0.645\text{M}$

7. What is the concentration of potassium dichromate if 8.00mL completely oxidizes 18.50mL of 3.00M iron II sulfate? Use the reaction as shown below. Show all work.



Answer: 1moles of $\text{Cr}_2\text{O}_7^{2-} = 6$ moles of Fe^{2+} .
 $0.0185\text{L} \times 3.00\text{M} = 0.055\text{moles Fe}^{2+}$, therefore $0.00925\text{moles Cr}_2\text{O}_7^{2-}$ used $(0.055\text{moles}/6)$.
 $0.00925\text{moles}/0.008\text{L} = 1.156\text{M}$

Post-lab:

1. Identify at least experimental 3 errors, excluding not following directions or incorrectly measuring volumes. What can be done to account for the errors you have noted in answer?

Answer: Students may suggest: a) proceeding too slowly with the reaction, b) allowing any of the solutions to be on the walls of the reaction vessels instead of in the reaction, c) not allowing the thermometer to stabilize, d) the room temperature is colder or warmer than temperature at which the solutions were allowed to equilibrate, e) the instruments used may be at different temperatures, therefore contributing or removing heat to the reaction f) heat generated from the stirring equipment g) potential evaporation from the surface of the liquid.

a) work quickly, but wait until the thermometer stabilizes, b) position the buret towards the center and not too high about the cups to prevent splashing; measure the acid directly into the cup and not drizzle along the side; or use a small amount of water to get the solution into the cup, c) allow solutions to stir in the cup and sit in the buret for a period of time to reach the temperature of the room, d) allow the instruments to sit at room temperature or warm them to room temperature, e) let the equipment equilibrate to room temperature, f) turn off stirring equipment when not in use to prevent heating, f) cover liquid to prevent evaporation.

1. What other factors influence the evolution of heat in the acid-base reactions; give at least 2 reasons? (Hint: you are not adding just pure acid or pure base to each other). How could you account for the factors you gave in answer?

Answer: Up to a certain concentration of acid or base, adding water to the acid or base will cause the evolution of heat. Adding a colder solution to the warmer solution will slightly drop the temperature of the solution, so if the reaction is done too slowly, this will affect the reaction greatly. Also, the strength of the acid or base used may affect the amount of heat given off in the reaction, in that the stronger the acid the more heat generated. The heat of reaction from the oxidation/reduction of these chemicals is significant enough to be observed. The heat observed in the experiment can be attributed to forming new bonds. Potentially the heat evolved could be increased by increasing the concentration of the reactants.

Knowing how much heat will be taken away by the addition of a cooler liquid and accounting the loss in heat. Knowing how much heat is generated by the addition of water to a concentrated base or acid, and accounting for this increase in temperature; this could be investigated by

looking at varying concentrations, c) The amount of energy required to break or make bonds will be required. Comparing various concentrations and looking at how much the temperature changes, and accounting for the heat change this way would account for differences in concentration.

2. If you used a diprotic acid, what would you expect the titration curve to look like for temperature vs. volume? Explain your reasoning.

Answer: If the titration is done carefully enough, it is possible to see multiple peaks in the curve indicating the removal of each proton. The graph should have two peaks.

Sample student responses:

- "If you were to use a diprotic acid then there would be two endpoints for the reaction because the reaction would take place in parts. The first hydrogen would dissociate then the second one would dissociate separately.
- "Diprotic acids have two acid protons. If a diprotic acid was used, I would expect the titration curve of temperature vs. volume to have two jumps in the graph due to two temperature changes."

3. Describe the reason for the shape of the graph.

Answer: The temperature will continue to increase significantly with the addition of the oxidizing agent/acid until the reaction is complete, and at this point the temperature reaches a maximum. The temperature drops because no more heat is generated and cooler liquid is being added. This causes the solution in the cup to drop in temperature.

5. Give a feasible reasoning for the evolution of heat from the redox titrations. How could you increase the heat evolved?

Answer: The heat of reaction from the oxidation/reduction of these chemicals is significant enough to be observed. The heat observed in the experiment can be attributed to forming new bonds. Potentially the heat evolved could be increased by increasing the concentration of the reactants.

1. Based on your experiment and the demonstration by your TA, which titration method is better and why? What are the advantages and disadvantages of each, and in what circumstances would you use one over the other. What other method can be used to perform titrations?

Answer: This is individual based (many answers will be correct and some wrong), but should be along the lines of using colorimetric when accuracy is not always needed, or when equipment not available. The thermometric is more accurate if done correctly and good for students with visual impairments. Another way to monitor would be to use a pH meter or conductivity meter.

2. What modifications would you make or suggestions to improve the efficiency of your titration, even if they are not feasible for a laboratory setting?

Answer: Potential answers can be using a purchased calorimeter, using another cup

Students were able to use the knowledge to develop sensible confirmatory questions, relate titrations to everyday life, and draw reasonable conclusions about the titration. Examples of students' responses include:

- "Is it possible to determine the concentration of the analytes in these titrations without using the titration method? Explain."
- "One reason for using titrations in the real/chemistry world is in pharmaceutical companies and how they need to neutralize or alter acids and bases for new medications."
- "With the one we looked at in class [thermometric titration] you have to just look at color and some people might not be able to see the change in color."

C&C responses to activity question 2 and 3 included the explanation of heat flow (to and from solution and surroundings), the temperature change observed, how this explained the enthalpy change observed, explaining that Styrofoam was an insulator hindering heat transfer between the solution and the surroundings while test tubes allow heat transfer freely between the solution and the surroundings.

"Because Styrofoam keeps the system isolated and traps the heat in therefore keeping coffee warmer longer." (C response).

Table F.2. Number of students with complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N) in the titration pre-lab questions.

Pre-lab Questions	Initial				Review			
	C&C	C	SC	N	C&C	C	SC	N
Question 1: Acid base strength (symbolizing and integrating).	74%	11%	0%	16%	84%	5%	0%	11%
Question 2a: Titration diagram (generalizing and specifying)	74%	0%	0%	26%	89%	5%	0%	5%
Question 2b: Conjugate pairs for reaction in Question 1.	63%	11%	16%	11%	68%	26%	5%	0%
Question 3a: Calculation using diagrams (integrating).	21%	21%	16%	42%	74%	16%	5%	5%
Question 3bi: Draw thermogram from data.	26%	58%	0%	16%	58%	32%	0%	11%
Question 3bii: Calculate ΔH_n and determine sign of enthalpy (problem solving).	63%	26%	11%	0%	84%	11%	5%	0%
Question 4ai: Balance equation.	63%	37%	0%	0%	74%	26%	0%	0%
Question 4aaii: Determine conjugate pairs (recognize).	42%	26%	21%	11%	79%	16%	0%	5%
Question 4aiii: Explain strength of conjugate base.	79%	0%	0%	21%	95%	0%	0%	5%
Question 4bi: Calculate concentration	89%	0%	0%	11%	89%	0%	0%	11%
Question 4bii: Calculate c_t	0%	0%	0%	100%	32%	0%	0%	68%
Question 4biii: Represent data in a diagram	53%	16%	5%	26%	63%	16%	0%	21%
Question 4biv: enthalpy	11%	32%	26%	32%	47%	11%	16%	26%

Table F.3. Average for each titration question of the pre-lab prior to and after the experiment.

Question	Points	Initial	Revision
		average	
Question 1: Acid base strength (symbolizing and integrating).	38	81%	88%
Question 2a: Titration diagram (generalizing and specifying)	10	72%	93%
Question 2b: Conjugate pairs for reaction in Question 1.	2	69%	80%
Question 3a: Calculation using diagrams (integrating).	25	40%	78%
Question 3bi: Draw thermogram from data.	3	57%	74%
Question 3bii: Calculate ΔH_n and determine sign of enthalpy (problem solving).	4	78%	91%
Question 4ai: Balance equation.	1	85%	91%
Question 4aii: Determine conjugate pairs (recognize).	1	52%	83%
Question 4aiii: Explain strength of conjugate base.	1	80%	94%
Question 4bi: Calculate concentration	4	85%	89%
Question 4bii: Calculate c_t	4	0%	32%
Question 4biii: Represent data in a diagram	16	65%	72%
Question 4biv: enthalpy	1	32%	56%

Table F.4. Percentage of complete and correct responses (C&C), correct but not complete (C), somewhat correct and incorrect (N).

Question	Points	C&C	C	SC	N	average
Activity						
1. Depict microscopically the chemicals before and after the reaction for the assigned reaction.	8	39%	22%	11%	28%	55%
2. Explain briefly how the flow of heat allows you to observe the enthalpy and temperature changes in these reactions.	6	17%	56%	6%	22%	49%
3. Based on your observation, explain why hot coffee is usually put in Styrofoam cups rather than glasses.	3	72%	6%	6%	6%	78%
Post lab						
1a. Correlation between titration and energy change.	18	28%	50%	11%	11%	60%
1bi. Determine if reaction is exothermic or endothermic.	6	17%	67%	6%	11%	60%
1bii. Correlation to pre-lab activity	4	33%	44%	6%	17%	57%
2a. Reverse order titration.	4	56%	17%	11%	17%	65%
2b. Diprotic titration.	3	39%	17%	17%	28%	56%
3ai. Conjugate pairs	15	39%	39%	0%	22%	59%
3aii. Pictorial titration representation.	2	22%	44%	0%	33%	44%
3b. Conjugate pair strength.	2	39%	28%	0%	33%	53%

Additional research data

The dilution of H₂SO₄ (10 mL solutions) showed that the dilution from 6 M to ~4 M was optimal (Table F.5.). The dilution results of HNO₃ were similar to those of H₂SO₄. The dissolution of NH₄ NO₃ produced a very cold solution with 0.1 – 1 g (Table F.6) and NH₄ Cl and KCl had similar results.

Table F.5. Sample observations of the dilution of H₂SO₄.

H ₂ SO _{4(aq)} + H ₂ O _(l) → H ₂ SO _{4(aq)} (Ambient temperature 23.2°C)		
Dilution	Observation (touch)	Temperature, °C
6 to 4M	Very warm	26.7
6 to 3 M	Warm	26.9
4 to 2 M	Slightly warm	24.8
3 to 1 M	Room temperature	24.5

Table F.6. Observation of temperature changes of dissolution reactions.

NH ₄ NO _{3(s)} + H ₂ O _(l) → NH ₄ NO _{3(aq)}		
Mass, g	Observation (touch)	Temperature, °C
0.056	Slightly cold	23.6
0.118	colder	23.3
0.519	Even colder	20.4
1.007	Very cold	20.6

Note: 1 mL water used for each sample; ambient temperature 28°C.

Derivation of c_m in the Styrofoam cups (constant-pressure calorimeter):

Equation 3.11-Equation F.6.

$$q_m = m_w c_w (T_f - T_i)$$

$$\text{where } \Delta T = T_f - T_i$$

$$q_h = m_w c_w (\Delta T)$$

$$: q_c = m_w c_w (\Delta T)$$

$$q_{cal} + q_h + q_c = 0;$$

where q_{cal} is the heat of calorimeter, which includes the medium (water) and the cups.

$$q_{cal} = -q_h - q_c$$

$$\therefore q_{cal} = c_m \Delta T$$

Equation F.1. Heat of cooling (mix hot + cold).

Equation F.2. Heat lost by hot water.

Equation F.3. Heat gained by cold water.

Equation F.4. Heat lost or gain in insulators.

Equation F.5. Heat of calorimeter.

Equation F.6. Resulting calorimetric equation.

References

1. Ragland, J.L. *Soil Sci. Soc. Am. Proc.* **1962**, 26, 133-7.
2. Williams, D. R. *Education in Chemistry*, **1971**, 8, 97-9.
3. Microsoft: *Choosing the best trendline for your data*, <http://office.microsoft.com/en-us/help/HP052623211033.aspx>; Last accessed June 2, 2008.
4. Papee, H. et.al, *Can. J. Chem.* **1956**, 34, 1677-1682.

Appendix G. Olfactory Acid-Base Titrations

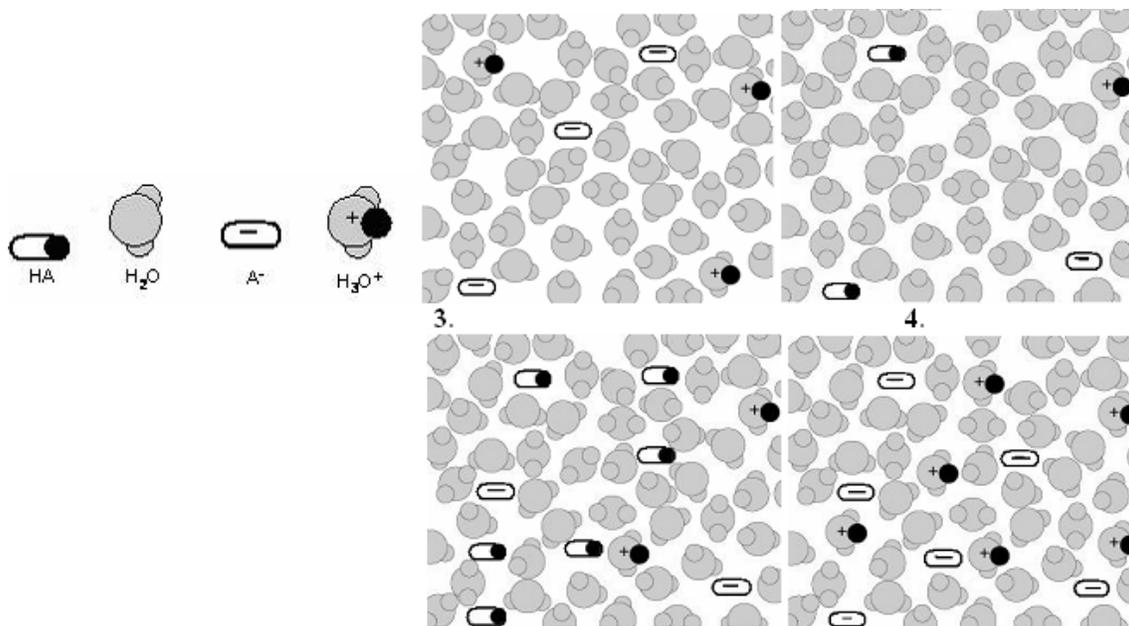
Learning Lab report: Olfactory Titration Pre-thoughts Questions

Name: _____ Lab section: _____ Lecture table #: _____
T.A.: _____ Group: _____ Date: _____

Note: These pre-lab questions **must** be completed before the lab and turned to the instructor on the date announced. **Read the entire experiment before answering these questions!** Read information in the text related to the topics: acids and bases, pH and concentration. Familiarize yourself with traditional acid-base titrations using color indicators.

Experimental procedure: Describe the experimental procedure in your *own* words (on another sheet). You may use any method you like such as bullet points, or diagrams. Be brief, but clear as this will be the procedure you will use to perform the experiment. You will not be allowed to use the experimental procedure handout in the lab. Review on the operation of the buret and pipet.

1. The diagrams below represent: a concentrated solution of a strong acid, a dilute solution of a strong acid, a concentrated solution of a weak acid and a dilute solution of a weak acid.¹



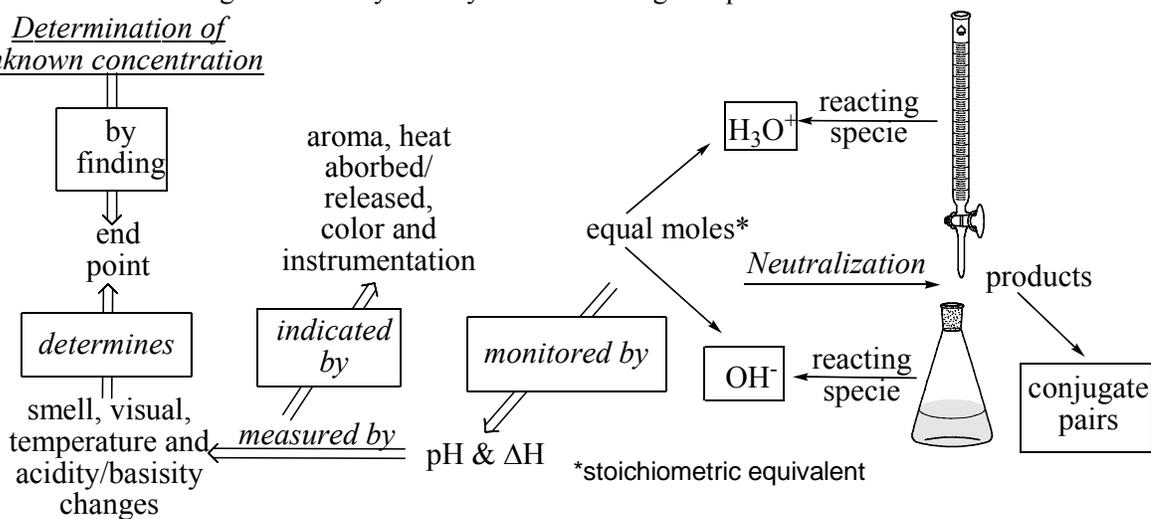
Indicate by the diagram number in the table below which diagram represents each of the four solutions. Briefly explain your answer giving an example of a strong and weak acid.

(¹Diagram adapted from Taber, K. S. Chemical misconceptions - prevention, diagnosis and cure, L: Volume 2: classroom resources, London: Royal Society of Chemistry, 2002.)

Acid	Strong: e.g. _____	Weak: e.g. _____
Concentrated	# _____ Explain:	# _____ Explain:
Dilute	# _____ Explain:	# _____ Explain:

2. With reference to the diagram below answer the following questions. You may add any information to the diagram that may assist you in answering the questions.

Determination of unknown concentration



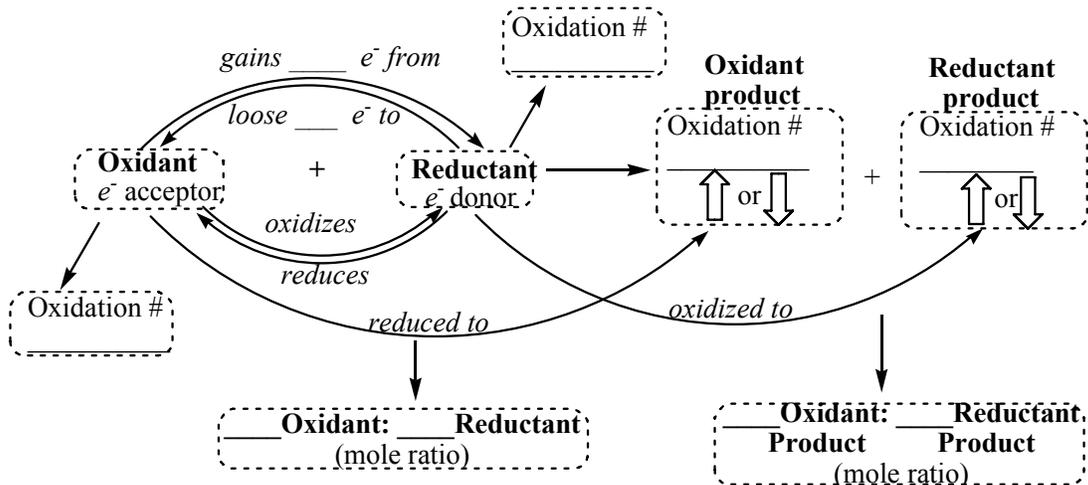
- a) High-light or circle the words in or areas of the diagram that **are not** associated with the olfactory titration you will be exploring.
- b) Briefly explain how aroma can be used to determine the H_3O^+ concentration in a *neutralization* reaction. Include a definition of neutralization (in your own words) as it relates to this diagram.
- c) Give the resulting conjugate acid-base pairs.
- How are conjugate pairs derived?
- Acid and conjugate base: _____
- Base and conjugate acid: _____

3. a) Write the full and ionic balanced equations for the acid-base reaction in the olfactory titration.

Full: _____ NaOH() + _____ HCl() → _____

Ionic: _____ () + _____ () → _____

b) Complete the redox definition diagram below and write the ionic equations for the redox reaction in the olfactory experiment below the diagram. Consult the Standard Reduction Tables.



Oxidant _____

Oxidant product _____

Reductant _____

Reductant product _____

Ionic equation:

You may use the conversion diagram and sample calculation table in Figure 1 below to answer the following questions. You may add to the diagram or develop your own calculation method, however all work *must be shown*.

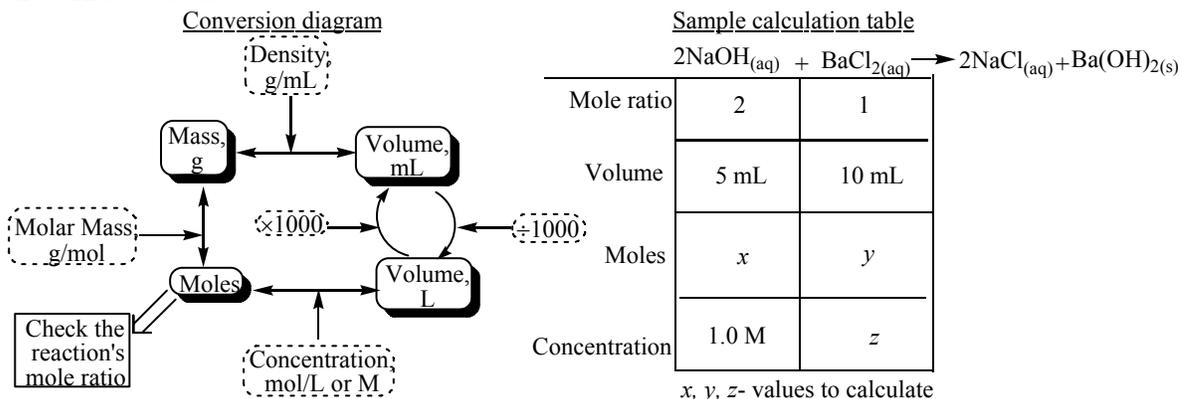
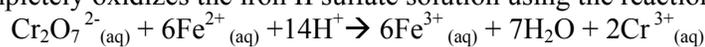
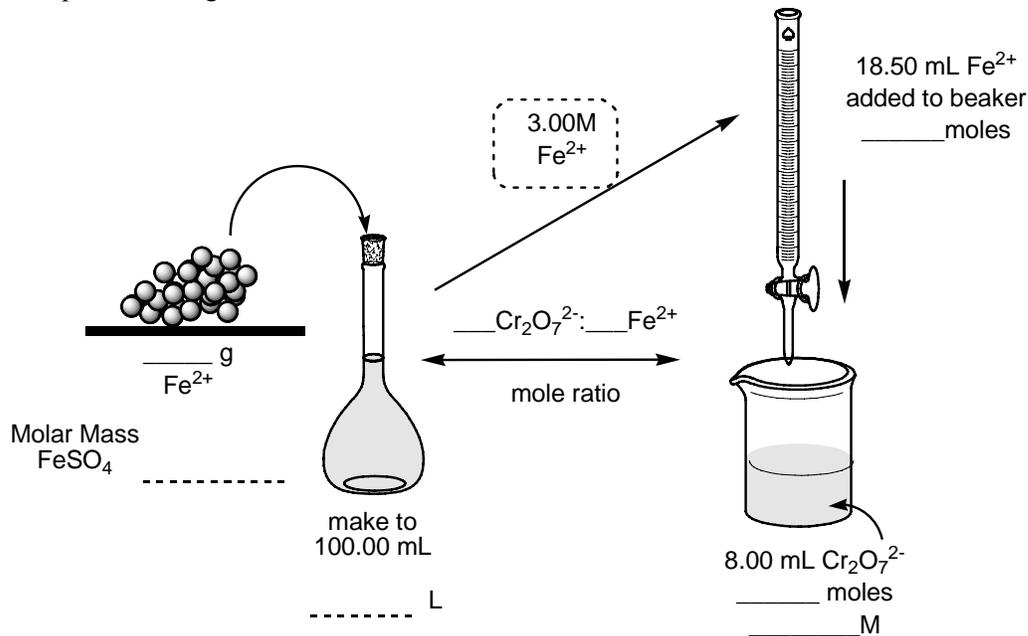


Figure 1. Conversion diagram and sample calculation table.

4. You make 3.0 M solution of iron II sulfate. You determine the concentration of potassium dichromate that completely oxidizes the iron II sulfate solution using the reaction as shown below.



Complete the diagram below to determine the concentration of dichromate and show all calculations.



5. You determine the concentration of NH₄Cl by performing a thermometric titration using 0.5 M KOH solution. You require 10.00 mL of the base to reach the end point to neutralize 5.0 mL of the acid.

- a) Write a balanced equation for the reaction. Indicate the conjugate acid and base. Is the conjugate base weak or strong? Explain briefly with reference to pre-lab question 1.
- b) Calculate the concentration of NH₄Cl. Draw a diagram similar to demonstrate titration including data given. Show all calculations below the diagram in question 4 or show your own method.

Olfactory Titrations using Rutabaga Indicator Experimental Procedure

Introduction: Titration is an analytical method used to determine the unknown concentration of an analyte from the known concentration of a titrant. The titrant is added to the analyte until a stoichiometric volume has been added to obtain the end point. The concentration of the analyte is determined from the known concentration and volume of the titrant at the end point. Olfactory titrations use the sense of smell to determine pH changes in the solution. The indicator solution is made from the rutabaga vegetable and aroma similar to like cabbage or potato is a result of isothiocyanates. An odorless compound found in the vegetable, glucosinolates, hydrolyzes to isothiocyanates in the presence of H_3O^+ .

Prerequisites: You should familiarize yourself with traditional acid-base titrations using color indicators. Review how to use titration data to calculation concentration.

Experimental inquiry: Utilize the sense of smell to determine the endpoint of a titration. Using the data, the concentration of your analyte will be determined.

Safety: Acids and bases are corrosive and may cause burn. Potassium permanganate may be flammable, causes *stains* and could cause burns. Consult the instructor about chemical spills and burns. Practice how to use the buret and pipet with water if you have never used them before. The TA can demonstrate proper techniques.

Procedure:

Part A. Observe and make notes on the colorimetric titration method demonstrated by your instructor. Record the reaction for this titration.

Part B. Determination of the end point of the olfactory titration of NaOH (standard solution) vs. HCl to find the percentage error.

1. Clean and thoroughly dry all glassware.
2. Obtain ~ 40 mL NaOH and HCl in two clean beakers.
3. Condition the pipet with a small amount of NaOH and the buret with HCl as shown in the “Volumetric Glassware” section of the “Introductory Material” of the lab manual. Before beginning, record the exact concentration written on the NaOH reagent bottle and use this value for future calculations.
4. Decide who will observe the aroma (O) and who will operated the buret to add the HCl (E).
5. Assemble the apparatus as in Figure 1, positioning the fan above the beaker, i.e. it must be blowing directly above and into the face of the observing student and *not on* the beaker. You **must** stand about **30 cm away** from the fan (use the markings on the bench).

6. Fill your buret with HCl ensuring the meniscus is no higher than the 0.00mL mark and record the volume. Measure 10.00 mL NaOH using the pipet into the beaker (Figure 1) and add 5 drops of the indicator solution.

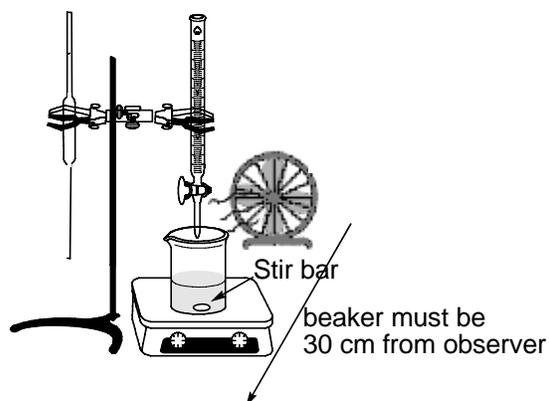


Figure 1. Olfactory titration apparatus.

7. Turn on the fan and E begins adding the HCl until an aroma is detected by O. Temporarily stop the titration at this volume. E should immediately tell O when the aroma is observed and continue observing the aroma at this volume for ~15 seconds to ensure the aroma is persistent. *If the aroma goes away immediately, add a little more HCl until it is persistent.*
8. Once an end point found, repeat the titration to obtain accuracy of the value. At least 3 trials must be performed. Work carefully, as the analysis needs to be within a 1% agreement for at least two volumes. Work slowly near the endpoint, so that this volume is not passed.
9. Obtain the exact HCl concentration from your instructor to determine your percent error. If there is a significant difference in concentrations, repeat your titration once more with more care.

Part C: Redox olfactory titration using known concentration of ceric ammonium nitrate to determine the concentration of ferrous ammonium sulfate hexahydrate (Fe^{2+}) in acid.

Repeat the same procedure using a known concentration of $\text{Ce}(\text{NH}_4)_4(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ solution as the titrant and measuring 10.0 mL of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ into the beaker as in Part B.

Part D: Clean-up

Wipe up any chemical spills. Dispose of chemicals in the corresponding waste containers. Rinse glassware with water and iron cleaning solution to remove any stains from Part C.

Post-Lab Report

Type or legibly write the results and responses to discussion questions. Answer the general questions in the spaces provided (write legibly).

Results and Discussion

1. Write balanced equations for the reactions in Parts A-C. Consult your pre-lab question #2.
2. Present the data for Parts B and C in tables as shown below (more rows will be needed). **Label** each table appropriately. Before leaving, all tables and the percentage error in Part B must be completed, and signed by the TA. Return all data with the post-lab report. **Note:** *Each page submitted must have your name, date, partner name(s) and TA name.*

Trial 1		Trial 2	
Volume, mL	Temperature, °C	Volume, mL	Temperature, °C
Use the two closest values from the graphs for the average: End point 1: _____ mL Acid End point 2: _____ mL Acid Average of 1 & 2: _____ mL Acid Concentration of NaOH: _____ M			TA Signature _____

3. Determine the average end point of each titration using the closest 2 values, indicating this in the tables. Calculate the unknown concentrations of acid and oxidizing agent. You may use tables or diagrams to aid your calculations as done in the pre-lab questions, but *show all work*.

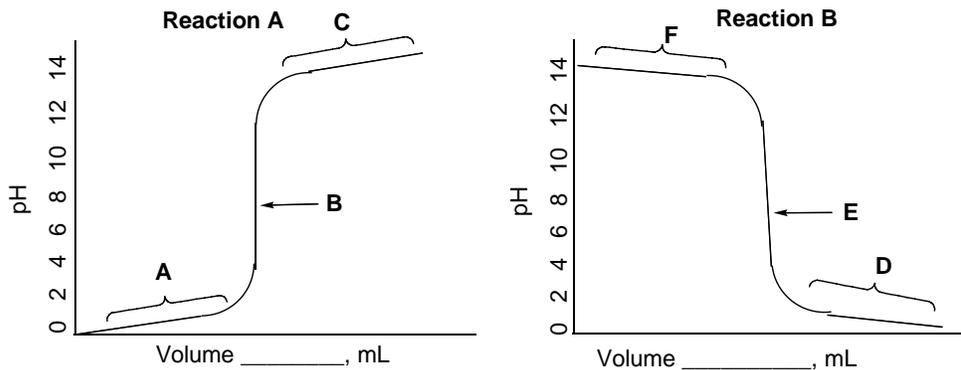
Conclusion (include these questions in the conclusions).

1. Identify at least experimental 3 errors, excluding not following directions or incorrectly measuring volumes. What can be done to account for the errors you have noted in answer?
2. Consider the experiment and the colorimetric titration demonstration by the TA, what are the advantages and disadvantages of titration and in what circumstances would you use each?
3. Give a practical application of titrations in the real world (be specific).
4. Re-examine your pre-lab answers. Have any of your original thoughts changed or been clarified? Make corrects to the pre-lab and submit the corrected pre-lab with a brief justification your changes.
5. Devise a plausible and thoughtful question related to this experiment (it should be sufficiently different from the questions given). This question may be chosen for discussion.

Name: _____ Lab section: _____ Lecture table #: _____
 T.A.: _____ Group: _____ Date: _____

Post-Lab Questions

1. The graphs below represent two different acid-base titrations. Indicate what is occurring in the beaker at the parts labeled A-F in terms of the H^+ and OH^- concentrations and observation of aroma with respect to pH during the titrations. Indicate in the diagram whether acid or base was being added.



	Acid and base reacted	Aroma Observed
A		
B		
C		
D		
E		
F		

2. a) What would happen to the temperature if 1mL portions of NaOH solution had been added to the beaker and the beaker contained the HCl and the indicator? Depict pictorially what is occurring at the microscopic and macroscopic levels.

b) What do you expect to happen if HCl was replaced with HBr in the original titration?

3. a) Complete the diagram below to depict the interaction of the reacting species in Part A that led to neutralization. Referring to the diagram, explain why the equivalence point will give the rutabaga aroma in this reaction.

NaOH(aq)

Before titration

During titration

HNO₃(aq)

produces

conjugate acid _____

conjugate base _____

Pay attention to the mole ratio!

Excess NaOH

Equivalence point

Legend

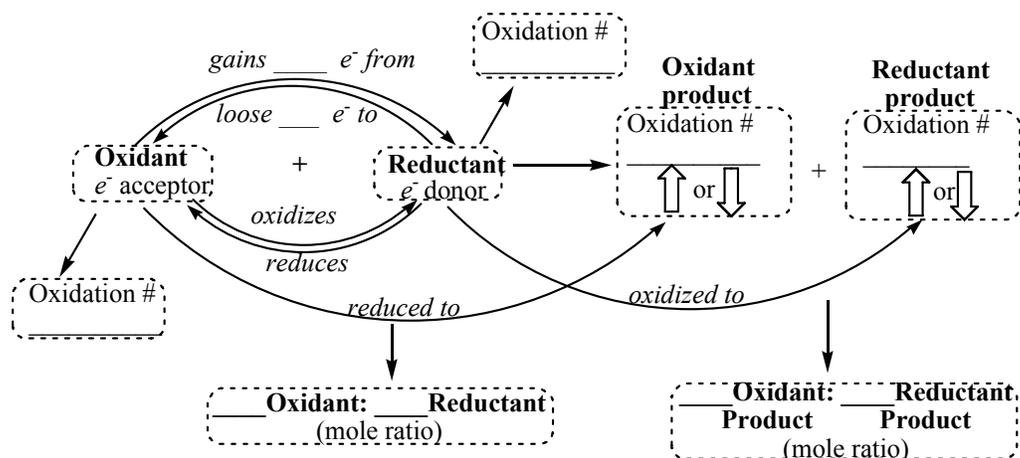
OH⁻ H⁺ NaOH H₂O

HNO₃ Na⁺ NO₃⁻

You may add other symbols but add them to the legend.

Explanation:

b) Is the resulting conjugate acid strong or weak? Why? Explain with reference to pre-lab question 1.



Oxidant

Oxidant product

4. Reductant

Reductant product

a) You were given KMnO_4 to replace the oxidant in the original titration when your lab partner dropped the bottle on the floor. Replace the bolded words in the diagram above with the reactants and products from this experiment by filling in the blanks below the diagram. Use the following questions to fill out the diagram:

i) Calculate and fill in the oxidation numbers of the reactants and products in the diagram.
Calculations:

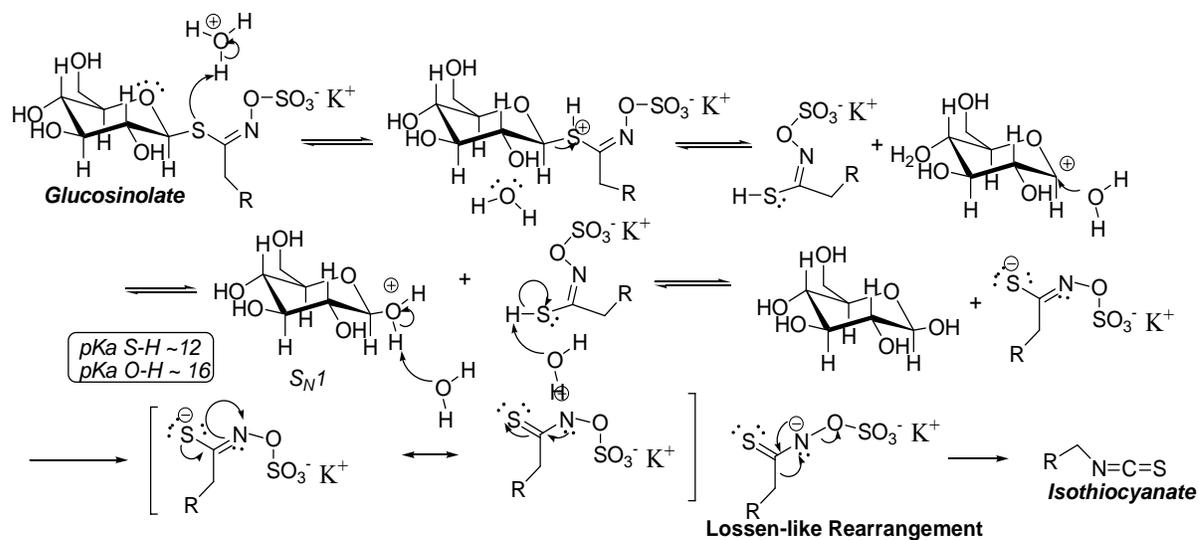
ii) Circle the arrows indicating if the oxidation number increased or decreased.

iv) Give the stoichiometric ratios between the reactants and the ratio between the products.

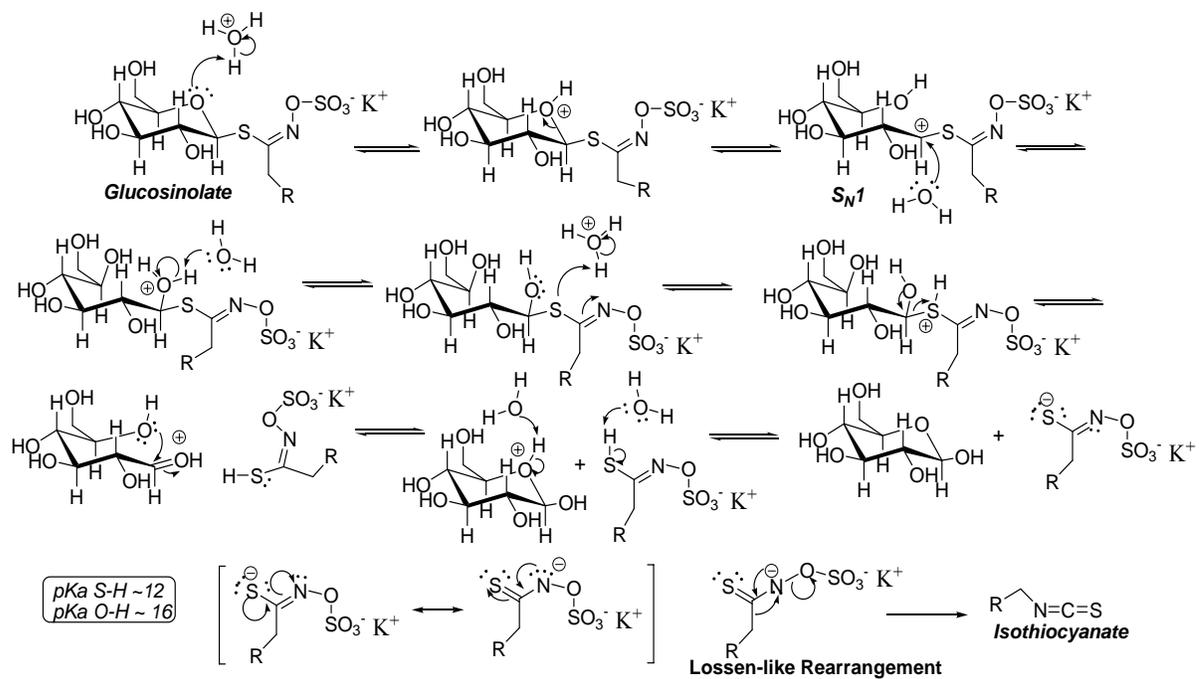
b) Write half-reactions and full *ionic* equations based on the answer in (a) (balance the equation and include states of matter). Consult the Standard Reduction Tables.

Half reactions:

Full ionic equation:



Scheme G.1. Proposed complete mechanism depicting C-S cleavage of glucosinolate.



Scheme G.2. Proposed complete mechanism depicting C-O cleavage of glucosinolate.