# CHEMTRAILS

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Chemistry 131 includes both lecture and laboratory work. To better understand chemistry, we believe you should become acquainted with fundamental principles and concepts and be able to apply them in the laboratory. Our goals in this course are to:

1) train you to think scientifically (develop curiosity),

2) train you to think analytically (solve problems),

3) provide you with scientific information of professional and social value,

4) prepare you for future science and engineering courses,

5) teach you basic chemical principles,

6) develop your ability to communicate scientific information,

7) provide you with laboratory experience.

As in most science or engineering courses, General Chemistry is difficult. To be successful, you must commit yourselves to academic excellence. You must diligently prepare for each class by reading the assigned portions of the text and working as many of the homework problems as you can, be attentive in class, and be willing to ask questions and seek extra instruction. You were selected for this course on your past academic experience and performance on the chemistry placement exam - you have the ability to do well in this course. The Chemistry faculty is here to assist you in doing the best you can.

Keep in mind that Chemistry is a 2 course unit, 6 semester hour course. You will receive twice the credit for this course as you would for the most of your other courses. You should therefore expect to spend twice as much time in preparation for Chemistry 131.

We hope you find this course interesting and informative; we know you will find it challenging.

## GENERAL POLICIES AND PROCEDURES

1. The schedule for Chemistry 131 is significantly different than other courses at the Academy. Check the syllabus daily. In general, you will have lectures on Monday, Wednesday, and Friday, one 2 hour lab on Tuesday and a 2 hour recitation on Thursday. If you have a question, be sure to consult your syllabus or ask your instructor. If in doubt, go to your classroom during the assigned period and check. Your instructor will clarify the schedule during the first lesson.

2. Do not schedule any appointments (dental, medical, EI, tailor shop, etc,) during any class or lab period.

3. If you know you will miss a class, inform your instructor at least one lesson in advance and submit a Form 78 before your absence if possible. You are responsible for all work assigned during your absence. If you miss a GR, you must take the make-up exam. If you will miss a GR due to a trip, inform your instructor at least a week in advance so he can coordinate with the OIC or OR for a make-up exam to be administered on the trip.

4. You must keep up with the course work even if you are hospitalized or on bedrest. If you need EI, notify the hospital liason officer to arrange EI with your instructor, or just call the Chemisty Department (x2960). Your instructor will give you EI if you are hospitalized for an extended period.

5. Do not leave the classroom or lab until you are dismissed by your instructor.

6. Please keep the classroom and coat closet clean and neat. Keep the doors to the coat closet closed when not in use - if you are the last to use it, close them. All outer garments (jackets, parkas, overcoats, overshoes, caps, etc.) must be neatly hung or stored in the coat closet - they are not permitted in the classroom.

7. Section Marcher Responsibilities:

a. Before Class. Maintain order in the classroom. Ensure the classroom and closet are neat and orderly. Collect any assignments due before the start of class.

b. Start of Class. Call the class to attention, render salute and report the class ready for instruction, and give your instructor all homework due. If your instructor does not arrive within 5 minutes after the start of class, report to the Chemistry Department for further instructions.

c. During Exams. If the instructor is absent during an exam, maintain order and give the command, "Cease Work," when the time has expired for the exam. The time should be written on the blackboard. Any cadet may give "Cease Work" when the time expires.

8. Classroom Materials. To each lecture class, you must bring your textbook, 3 ring binder, paper for taking notes, a pencil or pen, and a calculator (you will not be permitted to share calculators during quizzes or GRs). To each laboratory period, you must bring a pen (all experimental data must be recorded in ink) and your lab manual or handout for the lab.

9. Homework. In general, homework will not be collected or graded. Your instructor, however, has the option of collecting and grading your homework. The problems assigned indicate the knowledge level and proficiency expected of you. **At least 60% of all questions on the GRs and quizzes will be homework problems.**

10. Extra Instruction. Understanding of the material assigned is of the utmost importance. If you have difficulty, you should seek help immediately from the EI room (Room 2C56) or your instructor. The EI room is open from 0800 to 1600 every day unless otherwise noted. It will be closed during period M-5 and lunch.

11. Laboratory Experiments. Lab experiments supplement and reinforce the concepts covered in the classroom. They give you the opportunity to see chemistry in action. Here at the Academy, we do experiments in ways unfamiliar to you. Our experiments are performed at the microscale. With these experiments, we minimize student exposure to hazardous and toxic materials and reduce chemical waste. We are also able to perform more experimental work. While performing experiments, give SAFETY primary consideration. THINK BEFORE YOU ACT, ASK IF IN DOUBT.

**LAB REPORT FORMAT:**

A. All labs will include the following on the first page:

**Collaboration Statement:** State who you collaborated with on the lab. If no collaboration, state NO COLLABORATION. **FAILURE TO HAVE THIS SECTION WILL RESULT IN A 25% CUT ON THE LAB.**

B. For the Emission Lab, Enthalpy Lab, and the Spectrometric Determination of an Equilibrium Constant Lab the following format will be used:

**Collaboration Statement:** State who you collaborated with on the lab. If no collaboration, state NO COLLABORATION.

**Objective:** State the purpose or objective of the experiment in one sentence. The objective is chemical in nature; the objective is not to learn how to use an instrument.

**Theory:** In at least one full page (the equivalent of 1 full, typed double spaced page) discuss the theory governing the results of the experiment. The section generally begins with a short introduction detailing why you are doing this experiment, followed by a discussion of the procedures used to obtain the necessary data. To adequately write this section, you should consult your handout and/or textbook.

Do not simply copy another source. Compose this theory in your own words.

**Discussion of Results:** Answer the questions in the handout.

**Conclusion:** What can you conclude about the experiment? Give numerical results in the conclusion and error analysis.

C. For the remaining 75 point labs, the prelab exercise will be filled out BEFORE coming to class, the lab will be fill out during class and the conclusions will answered. Unless directed otherwise by your instructor, all lab reports will be due the Monday following the lab day. Only 4 of the 10 (75 point labs) will be graded. However, all must be completed and turned in or you will receive an INCOMPLETE FOR THE COURSE.

12. Late Work. All assigned work is due at the beginning of the period. Late penalties will be assessed according to the schedule below:

| | |
|---|---|
| < 1 lesson late | 25% |
| < 2 lessons late | 50% |
| > 2 lessons late | 100% |

Since Chemistry 131 does not follow the normal M/T-Day schedule, each class meeting (lecture or lab) is one lesson.

13. Computer Aided Instruction. You should have been issued three computer disks with chemistry computer aided instruction software. The instruction program descriptions are listed below:

| Disk | Programs |
|---|---|
| 1 | <u>The Elements</u>: Periodic Table, Nomenclature of the Elements, Isotopes/Atomic Weights, Properties of Some Elements, Mystery Element Quiz |
| | <u>Inorganic Nomenclature</u>: Binary Salts, Variable Oxidation State Salts, Binary Compounds of Two Nonmetals, Acids, Bases, Ternary Salts, Review Problems |
| | <u>Solutions</u>: Solubility, Solubility Experiment, Freezing Points, Molecular Weight Determination Experiment, Weight Percents, Molarity, Dilutions |
| 2 | <u>Atomic Formula and Molecular Weights</u>: Chemical Formulas, Atomic Weights, Molecular Formulas/Weights, Gram Molecular Weights, Gram/Mole Problems |
| | <u>Percent Composition and Empirical Formulas</u>: Introduction, Percent Composition, Empirical Formulas, Mg-HCl Experiment, Empirical Formula Problems |
| | <u>Chem Maze</u>: Arcade style game testing your knowledge of chemical reactions |

3 Chemical Formulas and Equations: Chemical Formulas, Chemical Equations, Writing Chemical Equations, Balancing Chemical Equations, Review Problems

Acids and Bases in Water: pH, Water, Strong Acids and Bases, Measuring pH, Neutralization, Acid-Base Titrations, Titration Experiment, Strong vs Weak Acids

Metric System: Prefixes, Temperature, Volume, Weight, Concentration, Density, Special Symbols and Functions

14. Additional CAI is available on the VAX-A computer via Falconnet. The programs and descriptions are as follows:

| Program | Description |
|---|---|
| Math | Tutorial on math and scientific notation |
| Logs | Tutorial and drill on logarithms |
| Names | Drill on chemical nomenclature |
| Namegame | Arcade-style nomenclature game (Bonus Points) |
| Mole | Mole concept and molecular weights |
| Limit | Tutorial and drill on limiting reagent problems |
| Thermo | Thermodynamic concepts and problems |
| Atom | Tutorial and drill on electronic structure |
| Force | Tutorial and drill on intermolecular forces |
| Gas | Tutorial and drill on gas laws |
| pH | Tutorial and drill on pH problems |
| Acid | Tutorial and drill on strong and weak acids |
| EMF | Tutorial and drill on electrochemical concepts |
| Qual | Dry run of qualitative analysis before the lab |
| Redox | Tutorial and drill on redox reactions |
| Chart | Tutorial on the periodic table, elements, etc. |
| Alchemy | A chemical knowledge adventure game (Bonus Points) |

We will give you information detailing the steps necessary to access the CAI software on the VAX-A.

15. Bonus Points from CAI. As you may have noticed from above, bonus points are available when playing NAMEGAME and ALCHEMY. Normally, Full Collaboration is permitted when using CAI. However, since points may be awarded for these two, INDIVIDUAL EFFORT is required. These games are available for use throughout the year, however, you may earn bonus points only during certain dates. We will give you additional information during the semester. Read instructions carefully when playing these games.

NAMEGAME is an arcade-style quiz where you give the correct name or chemical formula for elements and compounds. You are awarded 10 points for each correct answer and penalized 4 points for each wrong answer. You can play the game as many times as you desire, only your top score counts. Bonus points will be awarded to the top 30 scorers. NAMEGAME will be stopped at the end of Lesson T-21.

ALCHEMY is an arcade-style adventure game where you work your way through the land of Alchemy by overcoming adversaries with your knowledge of chemistry. ALCHEMY has ten levels you can progress through during the semester, earning up to 35 points for each successful completion of a level. The number of points you earn depends on the number of questions missed. You lose 10 points for the first question missed ("fatal encounter") and 5 points for subsequent missed questions. After missing a question, you're removed from the game and must reenter. If you miss more than 5 questions but finally complete the level, you earn 5 bonus points. Levels will be open for bonus points as we enter the block of material that is "tested" in them. Alchemy will be stopped at the end of Lesson T-42. The following is the schedule for the 10 levels of alchemy:

| Level Number | Opened | Closed |
|---|---|---|
| 1 | 10 Aug | 17 Aug |
| 2 | 10 Aug | 24 Aug |
| 3 | 24 Aug | 7 Sept |
| 4 | 7 Sept | 21 Sept |
| 5 | 21 Sept | 5 Oct |
| 6 | 5 Oct | 19 Oct |
| 7 | 19 Oct | 2 Nov |
| 8 | 2 Nov | 16 Nov |
| 9 | 16 Nov | 30 Nov |
| 10 | 30 Nov | 11 Dec |

**REMINDER: SINCE ALCHEMY AND NAMEGAME ARE PLAYED FOR POINTS, YOU MUST WORK ALONE.**

16. GRADING:

| | | |
|---|---|---|
| 4 GRs (300 pts/each) | | 1200 |
| 8 Course Quizzes (30 pts/each) | | 240 |
| 2 Instructor Pop Quizzes (30 pts/each) | | 60 |
| Lab Reports: | 4 @ 100 pts/each (Emission, Enthalpy, Determination of Kc, Qualitative Analysis) | 400 |
| | 4 @ 75 pts/each (4 of the remaining 10 labs will be graded randomly.) | 300 |
| Final | | 800 |
| **TOTAL** | | 3000 |

| Points for Prog | |
|---|---|
| 2 GRs | 600 |
| 2 100 pt labs | 200 |
| 2 75 pt labs | 150 |
| 3 quizzes | 90 |
| Prog Points | 1040 (35% of points) |

**Guaranteed Grade Cuts**

| | |
|---|---|
| Above 88% | Out of Final Exam (Including Alchemy and Namegame) |
| Above 80% | A |
| Below 50% | F |

## DFC COLLABORATION STATEMENT FOR INTRODUCTORY COURSES

**FULL COLLABORATION:** Collaboration is defined here to mean persons working together in joint intellectual effort. Collaboration does not include copying another's work. These assignments, prepared either inside or outside of class, may reflect collaboration with fellow students, faculty, or use of other sources. All such collaboration must be documented.

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# Chemistry 131 SYLLABUS Fall 1990

| Week | Date | Lesson No. USAFA | 131 | Topic | Reading | Homework |
|---|---|---|---|---|---|---|
| 1. | 9 Aug | M-1 | 1 | Matter and Measurement | 1.1-1.5 | 14,16,20,28,34 36,42,61 |
| | 10 Aug | T-1 | 2 | Atoms and Molecules | 2.1-2.6 | 1,2,6,8,12,18 25,38,40,49,58 |
| 2. | LAB: | Scientific | | Method ; Quiz #1 - 16 Aug | | |
| | 13 Aug | M-2 | 3 | Chemical Formulas | 3.1-3.5 | 3,5,13,17,22,30 |
| | 15 Aug | M-3 | 4 | Chemical Formulas | 3.6-3.8 | 31,32,38,43,49,51 |
| | 17 Aug | M-4 | 5 | Gases | 4.1-4.4 AFACT: 61-67 | 5,11,19,28,38,40, 44 |
| 3. | LAB: | Data Analyses | | | | |
| | 20 Aug | T-4 | 6 | Gases | 4.5-4.6 AFACT: 89-92 | 45,48,56,62,71 |
| | 22 Aug | T-5 | 7 | Electronic Structure | 5.1-5.3 | 4,8,11,14,20,22 |
| | 24 Aug | T-6 | 8 | Electronic Structure | 5.4-5.6 | 26,30,36,38,45 48,54 |
| 4. | LAB: | Emission; | | Quiz #2 - 30 Aug | | |
| | 27 Aug | M-7 | 9 | Electronic Structure | 5.7 AFACT: 133-150 | 64,66,68,78 |
| | 29 Aug | M-8 | 10 | Periodic Table | 6.1-6.4 | 5,6,11,14,16,22,24 |
| | 31 Aug | M-9 | 11 | Periodic Table | 6.5-6.6 | 28,30,38,42,60,63 |
| 5. | LAB: | NONE; | | GR #1 on Wednesday 5 Sep 90 | (Chap 1-6) | |
| | 5 Sep | M-10 | 12 | Thermochemistry | 7.1-7.2 | 4,8,10,14,18 |
| | 6 Sep | T-10 | 13 | Thermochemistry | 7.3-7.4 | 20,25,30,32,34,40 |
| | 7 Sep | M-11 | 14 | Thermochemistry | 7.5-7.7 | 49,50,55,56,60,68 |
| 6. | LAB: | Enthalpy | | | | |
| | 10 Sep | T-11 | 15 | Spontaneity of Reactions | 20.1-20.4 | 1,3,6,10,16,24,30, 34 |
| | 12 Sep | T-12 | 16 | Spontaneity of Reactions | 20.5-20.8 | 36,46,50,52,73 |
| | 14 Sep | T-13 | 17 | Covalent Bonding | 8.1-8.3 | 2,12,14,18,20,22, 26,28,34,42,48,60 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 7. | LAB: | Energy Simulator, Bring Geometry Kits to Lecture; Quiz #3 - 20 Sep | | | | |
| | 17 Sep | M-14 | 18 | Molecular Structure | 9.1-9.2 | 2,6,10,14,24,28 |
| | 19 Sep | M-15 | 19 | Molecular Structure | 9.3-9.5 | 32,37,40,44,46 |
| | 21 Sep | M-16 | 20 | Liquids and Solids | 10.1-10.2 | 2,4,6,8,15,16,20 |
| 8. | LAB: | Geometry, Bring Geometry Kits to Lab; Dr. Bartlett 25 Sep 90, 1900 | | | | |
| | 24 Sep | T-16 | 21 | Liquids and Solids | 10.3-10.5 | 22,24,27,32,34,36, 38 |
| | 26 Sep | T-17 | 22 | Liquids and Solids | 10.6-10.7 | 40,46,48,50,61,70 |
| | 28 Sep | T-18 | 23 | Solutions | 11.1-11.2 | 4,6,8,11,13,14,20 |
| 9. | LAB: | Solutions; GR # 2 on Tuesday 2 Oct 90 | | | (Chap 7-10, 20) | |
| | 3 Oct | M-20 | 24 | Solutions | 11.3-11.4 | 28,32,36,38,42,46 |
| | 4 Oct | T-20 | 25 | Air Pollution/Acid Rain | 19.5 | 46,47,63,64 |
| | 5 Oct | M-21 | 26 | Aqueous Reactions | 12.1-12.3 | 2,4,6,8,13,14,16, 18,22 |
| 10. | LAB: | Acid Rain ; Quiz # 4 - 11 Oct 90 | | | | |
| | 10 Oct | M-22 | 27 | Aqueous Reactions | 12.4-12.5 | 24,28,36,38,42,48, 64 |
| | 12 Oct | M-23 | 28 | Gaseous Equilibrium | 13.1-13.3 | 1,2,3,6,8,12,14,16 |
| 11. | LAB: | Determination of $K_c$; Quiz # 5 - 18 Oct 90 | | | | |
| | 15 Oct | T-23 | 29 | Gaseous Equilibrium | 13.4-13.5 20.7 | 18,28,36,38,43,44, 52,55,56,58 |
| | 17 Oct | T-24 | 30 | Acids and Bases | 14.1-14.2 | 5,6,12,16,24,28,30 |
| | 19 Oct | T-25 | 31 | Acids and Bases | 14.3-14.5 | 38,44,50,55,56,63, 69,78 |
| 12. | LAB: | Acid Base Titration; GR # 3 on Friday 26 Oct 90 (Chaps 11-15, 19.5) | | | | |
| | 22 Oct | M-26 | 32 | Acid Base/PPT Equilibria | 15.1-15.2 | 4,8,14,20,22,34 |
| | 24 Oct | M-27 | 33 | Acid Base/PPT Equilibria | 15.3 | 26,38,44,52,56,60 |
| | 26 Oct | M-28 | 34 | Chemistry of Photography Handout | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 13. | LAB: | Photography | | | | |
| | 29 Oct | T-28 | 35 | Qualitative Analysis | 17.1-17.3 | 1,2,3,6,12,16 |
| | 31 Oct | T-29 | 36 | Qualitative Analysis | 17.4-17.5 | 22,24,28,36,45,52 |
| | 2 Nov | T-30 | 37 | Rate of Reaction | 18.1-18.2 | 2,4,10,14,24,28 36,40,44 |
| 14. | LAB: | Qualitative Analysis; Quiz # 6 - 8 Nov 90 | | | | |
| | 5 Nov | M-31 | 38 | Rate of Reaction | 18.3-18.5 | 46,48,50 |
| | 7 Nov | M-32 | 39 | Rate of Reaction | 18.6-18.7 | 52,58,62,64 |
| | 9 Nov | M-33 | 40 | Atmosphere | 19.1-19.4 | 33,34,38,48,56, 67 |
| 15. | LAB: | Kinetics; Quiz # 7 - 15 Nov 90 | | | | |
| | 14 Nov | M-34 | 41 | Electrochemistry | 21.1-21.2 | 2,4,18,22,24,34 |
| | 16 Nov | M-35 | 42 | Electrochemistry | 21.3-21.4 | 46,48,58 |
| 16. | LAB: | None | | | | |
| | 19 Nov | T-35 | 43 | Electrochemistry | 21.5-21.6 | 60,67,68,69 |
| | 21 Nov | T-36 | 44 | Electrochemistry | 21.7 AFACT: 20-23 | 20,29,42 |
| 17. | LAB: | Electrochemistry; GR # 4 on Friday 30 Nov 90 (Chap 17-19,21) | | | | |
| | 26 Nov | M-37 | 45 | Organic Chemistry | 26.1-26.2 | 1,3,4,7,14 |
| | 28 Nov | M-38 | 46 | Organic Chemistry | 26.3-26.4 | 16,45,46,50 |
| | 30 Nov | M-39 | 47 | Organic Chemistry | 26.5-26.6 | 35,36,38,40,42 |
| 18. | LAB: | Organic; Quiz # 8 - 6 Dec 90 | | | | |
| | 3 Dec | T-39 | 48 | Polymers | 27.1-27.2 | 2,4,6,8,10,12 |
| | 5 Dec | T-40 | 49 | Polymers | 27.3-27.5 | 16,18,24 |
| | 7 Dec | T-41 | 50 | Applied Chemistry Option | | |
| 19. | LAB: | None | | | | |
| | 10 Dec | M-42 | 51 | Applied Chemistry Option | | |
| | 11 Dec | T-42 | | Clean-up | | |

# Chemistry 131 Labs Fall 1990

| WEEK | LAB No. | LAB | TYPE | GRADED* | POINT |
|---|---|---|---|---|---|
| 1 | | None (Transition Week) | - | - | - |
| 2 | 1 | Scientific Method | Micro | O | 75 |
| 3 | 2 | Data Analyses | In-Class | O | 75 |
| 4 | 3 | Emission | Macro | Y | 100 |
| 5 | | None (Labor Day) | - | - | - |
| 6 | 4 | Enthalpy | Macro | Y | 100 |
| 7 | 5 | Energy Simulator | DEMO | N | 0 |
| 8 | 6 | Geometry | In-Class | O | 75 |
| 9 | 7 | Solutions | Micro | O | 75 |
| 10 | 8 | Acid Rain | Micro | O | 75 |
| 11 | 9 | Determination of $K_c$ | Macro | Y | 100 |
| 12 | 10 | Acid Base Titration | Macro | O | 75 |
| 13 | 11 | Photography | Macro | O | 75 |
| 14 | 12 | Qualitative Analysis | Micro | Y | 100 |
| 15 | 13 | Kinetics | Micro | O | 75 |
| 16 | | None (Thanksgiving) | - | - | - |
| 17 | 14 | Electrochemistry | Micro | O | 75 |
| 18 | 15 | Organic | Macro | O | 75 |

* O - Optional
N - No
Y - Yes

Late Penalty:
< 1 lesson late 25%
< 2 lessons late 50%
> 2 lessons late 100%

L – LECTURE; R – RECITATION

# FALL SEMESTER 1990

| | SUNDAY | MONDAY | TUESDAY | WEDNESDAY | THURSDAY | FRIDAY | SATURDAY |
|---|---|---|---|---|---|---|---|
| | 29 | 30 | 31 | 1 | 2 | 3 | CADET WING RETURNS 2000 MOVES INTO FALL SQUADS 4 |
| 1 | LAB: 9 | 8 (---- FALL TRANSITION PERIOD ----) | 7 | 8 | M-1 L1 9 | T-1 L2 10 | 11 |
| 2 | SCI METHOD 12 | M-2 L3 13 | T-2 LAB 14 | M-3 L4 15 | T-3 R QUIZ #1 16 | M-4 L5 17 | 18 |
| 3 | DATA ANALYSIS 19 | T-4 L6 20 | M-5 LAB 21 | T-5 L7 22 | M-6 R 23 | T-6 L8 24 | 25 |
| 4 | EMISSION 26 | M-7 L9 27 | T-7 LAB 28 | M-8 L10 29 | T-8 R QUIZ #2 30 | M-9 L11 31 | HOME CSU 1 (- PARENTS' WEEKEND -) |
| 5 | NONE 2 (----) | HOLIDAY LABOR DAY 3 | T-9 R 4 | M-10 L12 GR #1 5 | T-10 L13 6 | M-11 L14 7 | HOME HAWAII 8 |
| 6 | ENTHALPY 9 | T-11 L15 10 | M-12 LAB 11 | T-12 L16 12 | M-13 R 13 | T-13 L17 FATIGUES/BDU WARFIGHTING AWARE 14 | HOME CITADEL 15 |
| 7 | ENERGY SIMULATOR 16 | M-14 L18 17 | T-14 LAB 18 | M-15 L19 19 | T-15 R QUIZ #3 20 | M-16 L20 21 | AWAY WYOMING 22 |
| 8 | GEOMETRY 23 | T-16 L21 24 | M-17 Dr. Bartlett LAB 25 | T-17 L22 26 | M-18 COMP TIME 27 | T-18 L23 28 | AWAY SDSU 29 |
| 9 | SOLUTIONS 30 | M-19 R 1 | T-19 LAB GR #2 2 | M-20 L24 3 | T-20 L25 4 | M-21 L26 5 | HOME NAVY 6 |
| 10 | ACID RAIN 7 | HOLIDAY COLUMBUS DAY 8 | T-21 LAB 9 | M-22 L27 10 | T-22 R QUIZ #4 11 | M-23 L28 FATIGUES/BDU WARFIGHTING AWARE 12 | AWAY NOTRE DAME 13 |
| 11 | DETER-MINE $K_c$ 14 | T-23 L29 15 | M-24 LAB 16 | T-24 L30 17 | M 25 R QUIZ #5 18 | T-25 L31 19 | OPEN 20 |
| 12 | A/B TITRATION 21 | M-26 L32 22 | T-26 LAB 23 | M-27 L33 24 | T-27 R 25 | M-28 L34 GR #3 26 | HOME UTAH 27 |
| 13 | PHOTO-GRAPHY 28 | T-28 L35 29 | M-29 LAB 30 | T-29 L36 31 | M-30 R 1 | T-30 L37 2 | HOME BYU 3 |
| 14 | QUALI-TATIVE ANALYSIS 4 | M-31 L38 5 | T-31 LAB 6 | M-32 L39 7 | T-32 R QUIZ #6 8 | M-33 L40 FATIGUES/BDU WARFIGHTING AWARE 9 | AWAY ARMY 10 |
| 15 | KINETICS 11 | HOLIDAY VETERAN'S DAY 12 | T-33 LAB 13 | M-34 L41 14 | T-34 R QUIZ #7 | L42 16 | AWAY UTEP 17 |
| 16 | NONE 18 | T-35 L43 19 | M-36 R 20 | T-36 L44 21 | 22 (---- THANKSGIVING WEEKEND ----) | 23 | 24 |
| 17 | ELECTRO-CHEM 25 (----) | M-37 L45 26 | T-37 LAB 27 | M-38 L46 28 | T-38 R 29 | M-39 L47 GR #4 30 | 1 |
| 18 | ORGANIC 2 | T-39 L48 3 | M-40 LAB 4 | T-40 L49 5 | M-41 R QUIZ #8 6 | T-41 L50 7 | 8 |
| | 9 | M-42 10 | T-42 CLEANUP 11 | STUDY DAY 12 | FINALS 1/2 13 | FINALS 3/4 14 | FINALS 5/6 15 |
| | STUDY DAY 16 | FINALS 7/8 17 | FINALS 9/10 18 | FINALS 11/12 19 | 20 (---- CHRISTMAS BREAK ----) | 21 | 22 |

FALL SEMESTER 1990 (CHEPC/2585)

APPROVED BY ACADEMY BOARD: 20 MAY 89

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# INORGANIC NOMENCLATURE
## Chemistry 131

Chemistry is a lot like living in a foreign country. If you speak the language, life is more fun! Learning inorganic nomenclature is the first step toward learning the language of chemistry. Learning the relationship between chemical formulas and chemical names is essential for understanding chemical problems. Inorganic nomenclature is a systematic way of naming the thousands of inorganic compounds which we encounter.

Your textbook discusses nomenclature of inorganic compounds on pages 72-78. This handout is intended to supplement and complement your book. Another source of nomenclature rules and practice in the CAI lesson NAMES. Contact your instructor if you want a copy.

**BEFORE WE GET STARTED . . .**

There are certain elements, cations, and anions that you MUST know before you get started. MEMORIZE these names and formulas; it's as simple as that! For any name you should be able to write the formula and for any formula you should be able to write the name (including spelling.)

1. The first 36 elements and Au, U, Ag, Sn, Hg, and Pb.

2. Compounds with common names

   $H_2O$ - water
   $H_2O_2$ - hydrogen peroxide
   $NH_3$ - ammonia

3. Cations

| Names | Symbol |
|---|---|
| Lithium ion, sodium ion, etc. | $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$ |
| Beryllium ion, magnesium ion, etc. | $Be^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$ |
| Hydronium ion | $H^+$ |
| Aluminum(III) | $Al^{3+}$ |
| Iron(II), Iron(III) | $Fe^{2+}$, $Fe^{3+}$ |
| Copper(I), Copper(II) | $Cu^+$, $Cu^{2+}$ |
| Silver(I) | $Ag^+$ |
| Mercury(I), Mercury(II) | $Hg_2^{2+}$, $Hg^{2+}$ |

| | |
|---|---|
| Lead(II), Lead(IV) | $Pb^{2+}$, $Pb^{4+}$ |
| Ammonium | $NH_4^+$ |

4. Common Monatomic Anions

| Name | Symbol | Name | Symbol |
|---|---|---|---|
| Hydride | $H^-$ | Iodide | $I^-$ |
| Fluoride | $F^-$ | Oxide | $O^{2-}$ |
| Chloride | $Cl^-$ | Sulfide | $S^{2-}$ |
| Bromide | $Br^-$ | | |

5. Common Polyatomic Anions (Two or more atoms)

| Name | Formula | Name | Formula |
|---|---|---|---|
| Nitrate | $NO_3^-$ | Sulfate | $SO_4^{2-}$ |
| Permanganate | $MnO_4^-$ | Carbonate | $CO_3^{2-}$ |
| Hydroxide | $OH^-$ | Chromate | $CrO_4^{2-}$ |
| Cyanide | $CN^-$ | Phosphate | $PO_4^{3-}$ |
| Perchlorate | $ClO_4^-$ | Peroxide | $O_2^{2-}$ |
| Thiocyanate | $SCN^-$ | Chlorate | $ClO_3^-$ |

6. Acids

| | | | |
|---|---|---|---|
| Sulfuric | $H_2SO_4$ | Perchloric | $HClO_4$ |
| Phosphoric | $H_3PO_4$ | Chloric | $HClO_3$ |
| Nitric | $HNO_3$ | Hydrobromic | HBr |
| Hydrochloric | HCl | Hydroiodic | HI |

7. Bases

| | | | |
|---|---|---|---|
| Lithium hydroxide | LiOH | Magnesium hydroxide | $Mg(OH)_2$ |
| Sodium hydroxide | NaOH | Calcium hydroxide | $Ca(OH)_2$ |
| Potassium hydroxide | KOH | Strontium hydroxide | $Sr(OH)_2$ |
| Cesium hydroxide | CsOH | | |
| Rubidium hydroxide | RbOH | | |

There are four main classes of inorganic compounds we will learn how to name:

1. Compounds made from single valence metals.
2. Compounds made from multivalent metals.
3. Compounds containing only nonmetallic elements.
4. Acids.

COMPOUNDS MADE FROM SINGLE VALENCE METALS

In general, these compounds are made using at least one of the metals in Groups IA and IIA. These metals donate electrons readily (they have a low ionization energy) and always have oxidation numbers corresponding to their group number. For example, K, Na, Cs, etc., have oxidation numbers of +1 only. All we have to do is specify the cation (the ionic metal) followed by the anion. We must also ensure that the sum of the oxidation numbers is zero (for we are dealing with neutral molecules). Here are some examples:

| | |
|---|---|
| NaH | sodium hydride |
| $Cs_2O$ | cesium oxide |
| $BaF_2$ | barium fluoride |
| HCN | hydrogen cyanide |
| $Sr_3N_2$ | strontium nitride |
| $Ca(OH)_2$ | calcium hydroxide |
| $Li_3PO_4$ | lithium phosphate |
| $MgSO_4$ | magnesium sulfate |

Now, you try a couple!

a. $Na_2CrO_4$ _____

b. magnesium fluoride _____

In question (a), the cation is $Na^+$ (sodium) and the anion is $CrO_4^{2-}$ (chromate). Thus, the compound is sodium chromate. In question (b), magnesium exists in compound form as $Mg^{2+}$. Fluoride is the $F^-$ anion. To make the compound neutral, we need two $F^-$'s. Therefore, the formula for magnesium fluoride is $MgF_2$.

If we have an ionic compound that contains hydrogen along with the cation, then we need to specify the number of hydrogen atoms in the compound. For instance,

| | |
|---|---|
| $NaHCO_3$ | sodium hydrogen carbonate |
| $Na_2HPO_4$ | sodium monohydrogen phosphate |
| $NaH_2PO_4$ | sodium dihydrogen phosphate |

In the above examples, we use Greek prefix before the word "hydrogen"

to specify the number of hydrogens. In case you've forgotten, here are the prefixes:

| | | |
|---|---|---|
| mono- | 1 | (Omitted if no other prefixes are used) |
| di- | 2 | |
| tri- | 3 | |
| tetra- | 4 | |
| penta- | 5 | |
| hexa- | 6 | |
| hepta- | 7 | |
| octa- | 8 | |
| nona- | 9 | |
| deca- | 10 | |

Notice that for $NaHCO_3$, the number of hydrogens is not specified.

This is because carbonate has a -2 charge; if sodium ($Na^+$) combines with $CO_3^{2-}$, there is only "room" for one hydrogen. Thus, the mono- is inferred in this case.

COMPOUNDS MADE FROM MULTIVALENT METALS (STOCK SYSTEM)

Nonionic metals can usually have more than one oxidation state. Iron, for instance, can be found as $Fe^{3+}$ and as $Fe^{2+}$. Most other transition metals can also assume more than one oxidation state. The way we distinguish between compounds which differ in oxidation numbers is by using Roman numerals, which is known as the Stock system. The Roman numeral indicates the oxidation number of the cation and is enclosed in parentheses immediately after the metal name. Take a look at these examples:

| | |
|---|---|
| $FeSO_4$ | iron(II) sulfate |
| $Fe_2(SO_4)_3$ | iron(III) sulfate |
| $PbO_2$ | lead(IV) oxide |
| $Sn(NO_3)_2$ | tin(II) nitrate |
| $CuCN$ | copper(I) cyanide |
| $Hg(OH)_2$ | mercury(II) hydroxide |

Note the sum of the oxidation numbers(s) of the metal exactly cancels the sum of the negative charge(s) of the anion. Note also that you need <u>not</u> memorize the oxidation number of the metal because you can always back calculate its value by knowing the charge on the anion. In other words, memorize the anions, both name and charge.

Let's try a couple!

a. $CuSO_4$ _____

b. iron(III) carbonate _____

In (a), remember to key off the anion! Since you've already memorized (?) the anions, you know that sulfate has a -2 charge. To make the compound neutral, you know that copper must have a +2 charge. Since copper is multivalent, we will express its oxidation state when we name the compound: copper(II) sulfate. For (b), the (III) tells us that the iron is in the +3 state ($Fe^{3+}$). We know from our memorized list of anions that carbonate has a -2 charge ($CO_3^{2-}$). To make a neutral iron(III) carbonate formula, we must balance the negative and positive charge. Two $Fe^{3+}$'s and three $CO_3^{2-}$'s would balance the charge at +6 and -6: $Fe_2(CO_3)_3$.

As with most topics in chemistry, there are always some exceptions. A number of metals exist which are not in Groups I or II and have one oxidation state. For these compounds you do not specify the oxidation state in parenthesis. The exceptions you should know are Ag(+1), Ni(+2), Zn(+2), and Al (+3). Here's some examples of what we're talking about:

| | |
|---|---|
| $AgMnO_4$ | silver permanganate |
| $Ni(ClO_4)_2$ | nickel perchlorate |
| $AlH_3$ | aluminum hydride |

Remember, we used no Roman numerals in naming these exceptions. Note also that most transition metals can exhibit a +2 ion due to ionization of the 2s electrons.

## COMPOUNDS CONTAINING ONLY NONMETALLIC ELEMENTS

Let's move to the opposite end of the periodic table. Here we find the nonmetallic elements which are defined as having a high (negative) electron affinity. In general, the nonmetallic elements include those elements to the right and above the dark, solid stair-step line on the periodic table that forms a diagonal from boron (B) to astatine (At). Compounds formed solely from these elements will be covalent in nature. When naming these molecules, we use Greek prefixes because the oxidation number or each element is not always obvious. The compound name begins with the most electropositive atom (the least electronegative) and then the other element is named (once again with the "ide" ending as in the anion). Let's look at some examples:

| | |
|---|---|
| $CBr_4$ | carbon tetrabromide |
| $PF_3$ | phosphorus trifluoride |
| $N_2O_5$ | dinitrogen pentoxide |
| $XeF_6$ | xenon hexafluoride |

Here are a couple for you to try!

a. NO _____

b. sulfur hexafluoride _____

The formula in (a) is nitrogen monoxide. If there is only one of the more electropositive atoms, the "mono-" prefix can be dropped. The "mono-" prefix is always used for the more electronegative atom. In (b), no prefix on the sulfur implies one sulfur. Hexafluoride means six F⁻'s. Therefore, the formula is $SF_6$.

ACIDS

As a final note, we should talk about naming acids. You should be familiar with some common names, such as the following:

$HNO_3$ nitric acid

$H_2SO_4$ sulfuric acid

All oxyacids (acids containing oxygen) are named after the name of the anion. For example,

| | |
|---|---|
| $HClO_4$ | perchloric acid (from perchlorate ion) |
| $HClO_3$ | chloric acid (from chlorate ion) |
| $H_2CrO_4$ | chromic acid (from chromate ion) |

Other acids have the same formula as some of the compounds discussed above but have a different name.

| | |
|---|---|
| HCl(aq) | hydrochloric acid |
| HBr(aq) | hydrobromic acid |
| HF(aq) | hydrofluoric acid |
| HCN (aq) | hydrocyanic acid |

Most of the time we will add the abbreviation for aqueous (aq) after the compound to indicate that it is dissolved in water and is, therefore, an acid. For instance, HI(aq) would be called hydroiodic acid where as HI would be termed hydrogen iodide.

Nomenclature is an important part of the language of chemistry. Get use to naming these compounds. You'll be seeing much more of them throughout the year!!!

The next page is a nomenclature work sheet. Use this to help you practice your nomenclature skills!!!

## NOMENCLATURE WORK SHEET

Now, let's see how much you've learned! Use the following to practice your nomenclature skills!!!

**Name the following:**

| | | | |
|---|---|---|---|
| $(NH_4)_2CO_3$ | _____ | $N_2O$ | _____ |
| $P_4O_6$ | _____ | $H_2SO_4$ | _____ |
| $Al_2O_3$ | _____ | $SnCl_4$ | _____ |
| $BaCl_2$ | _____ | $NaH$ | _____ |
| $Cu_2S$ | _____ | $MnS$ | _____ |
| $KHSO_4$ | _____ | $BeSO_4$ | _____ |
| $CO_2$ | _____ | $HBr$ | _____ |
| $(NH_4)_2HPO_4$ | _____ | $PF_5$ | _____ |
| $Fe_2O_3$ | _____ | $P_4O_{10}$ | _____ |
| $Ca(MnO_4)_2$ | _____ | $HClO_4$ | _____ |

**Give formulas for the following:**

| | | | |
|---|---|---|---|
| ammonium sulfate | _____ | barium iodide | _____ |
| calcium oxide | _____ | sodium sulfide | _____ |
| potassium permanganate | _____ | iron(II) sulfate | _____ |
| silver phosphate | _____ | sulfur trioxide | _____ |
| copper(II) oxide | _____ | aluminum sulfide | _____ |
| magnesium iodide | _____ | carbonic acid | _____ |
| titanium(IV) chloride | _____ | vanadium(V) oxide | _____ |

# Scientific Method
## Chemistry 131

**OBJECTIVE**

To become proficient in using the scientific method. This lab will lead you through the scientific method of problem solving. You will make observations, examine your observations for patterns, make and verify hypotheses, perform experiments that were designed for you, and design your own experiments. Finally, you will be able to determine the reaction pathway for a "clock reaction."

**INTRODUCTION**

Francis Bacon suggested centuries ago that as a result of careful observation of phenomena there would always emerge a logical explanation; others believe that aimless experimentation without a preconceived objective leads nowhere. The scientist works in two directions: he collects data and from his observations he proposes explaining hypotheses through a process of induction, then he seeks to verify this explanation through a process of deduction. It is the rare scientist who has enough imagination to create new valid hypotheses. Most scientists just "get mileage" out of someone else's hypotheses by doing variations of his experiments. It was forty years after noted theoretician Albert Einstein proposed the conversion of mass to energy that the invention of the atomic bomb validated his hypothesis.

The inductive method propelled science to prominence during the Enlightenment period of the Renaissance. Previously the ancient Greeks worked entirely through deduction and the fiction of the four "elements" (Earth, Air, Fire, and Water). Later, the pursuit of the "Materia Prima" by Alchemists testified to the futility of a purely deductive process that begins with an idea and denies the results of any experiment which does not turn out as predicted. (1)

Modern science dates from the sixteenth century when systematic observation and experiment developed the inductive part of the process. The formation of a hypothesis is an attempt to guess why something happens, hence it is inductive. Deductive prediction of results leads to verification when the hypothesis is tested. Repeated observation-prediction-verification-revision of a hypothesis leads to an acceptable explanation called a theory. This approach, in its simplest form, consists of several distinct steps:

1. **Making observations.** The observations may be qualitative (the sky is blue, BCT is fun) or quantitative (the pressure is 1 atmosphere; the temperature is 21° C). Many chemical reactions involve changes in color, evolution of a gas, or formation of a precipitate. However, not all reactions occur instantly, some take minutes, hours, days, or even years. (2)
2. **Looking for patterns in the observation.** This process often results in the formation of a **natural** or **scientific law.** For example, studies of countless chemical reactions have shown that the substances present after a reaction have the same total mass as that

of substances present before the reaction took place. These observations can be generalized as the law of conservation of mass. (2)

3. **Formulating theories.** A theory consists of a set of assumptions put forth to explain the observed behavior of matter. At first, the set of assumptions is called an **hypothesis**. If the tentative hypothesis survives the tests of many experiments, we gain confidence in its value and call it a theory. At this time, it is important to distinguish between an observation and a theory. An observation is a fact that endures time, while a theory is an interpretation and may change when more facts are known. (2)

4. **Designing experiments to test the theories.** Typically, science is self-correcting, continuously testing its theories. We must continue to do experiments and refine our theories in light of new observations if we hope to approach a more correct understanding of natural phenomena. (2)

When designing an experiment that involves several variables, one must change only one variable at a time. If you were to change two variables for the same experiment, it would be impossible to determine which of the changed parameters caused the change in the observation.

The preceding discussion describes the ideal scientific method. However, it is important to understand that science does not always progress smoothly and efficiently. Scientists are human: They have prejudices; they misinterpret data; they become emotionally attached to their theories and become non-objective. The scientific method is only as effective as the humans using it. It does not automatically lead to progress.

This experiment is designed to give you some practice in the ways of scientists. The scientist observes results of procedures, makes hypotheses to explain these results, verifies the hypotheses, designs experiments to isolate one variable, and finally assembles a theory about the reaction. The chemical reaction that we are investigating is called a "clock reaction." Chemicals are mixed and after an interval of several minutes the sudden appearance of a blue color signals the completion of the process--a chemical reaction has taken place. You will first carry out some simple combinations of solutions, record the results, and try to explain in chemical terms why changes occur. As successive steps become more complex, look for consistent patterns and exceptions, verify changes, and finally try to put together a description of the processes which together make up the clock reaction.

**Experimental Information**

1. Clean the pipets before and after the lab.

2. Keep the pipets used for the iodine solution separated from the rest. Iodine will stain the pipets and we want to minimize the number of pipets we stain.

**Procedure:**

Record all observations and your explanations in the space provided. Be sure to observe all reactions for at least 10 minutes before assuming nothing has happened. Do not stir the solutions after initial mixing.

1. Place about 3 drops of KI (potassium iodide), KCl (potassium chloride), $(NH_4)_2S_2O_8$, (ammonium peroxydisulfate), $Na_2S_2O_3$ (sodium thiosulfate), and $I_2$ on separate locations of your reaction surface. Add 1 drop of starch solution to each of these solutions. Record your observations below.

| | Solution | Observation |
|---|---|---|
| a. | KI, starch | _____ |
| b. | KCl, starch | _____ |
| c. | $(NH_4)_2S_2O_8$, starch | _____ |
| d. | $Na_2S_2O_3$, starch | _____ |
| e. | $I_2$, starch | _____ |

Starch indicates the presence of what species? _____

2. Try various combinations of the solutions used in Step 1, taking them two at a time (use about 3 drops each). Then add 1 drop of starch to each. Which combinations give a positive result (appearance or disappearance of a blue color)? This is a key step in analyzing the reaction.

| | Solution | Observation |
|---|---|---|
| a. | KI, KCl, starch | _____ |
| b. | KI, $(NH_4)_2S_2O_8$, starch | _____ |
| c. | KI, $Na_2S_2O_3$, starch | _____ |
| d. | KI, $I_2$, starch | _____ |
| e. | KCl, $(NH_4)_2S_2O_8$, starch | _____ |
| f. | KCl, $Na_2S_2O_3$, starch | _____ |
| g. | KCl, $I_2$, starch | _____ |
| h. | $(NH_4)_2S_2O_8$, $Na_2S_2O_3$, starch | _____ |
| i. | $(NH_4)_2S_2O_8$, $I_2$, starch | _____ |
| j. | $Na_2S_2O_3$, $I_2$, starch | _____ |

3. On separate areas on the reaction surface place:

(a) 3 drops of KI
(b) 3 drops of KI and 1 drop of $Na_2S_2O_3$
(c) 3 drops of KCl

To each of these, add 1 drop of starch. Then add 3 drops of $(NH_4)_2S_2O_8$. Record your results below and explain why you think a positive result was or was not obtained. What seemed to be the effect of $Na_2S_2O_3$?

| Solution | Observation |
|---|---|
| a. KI, $(NH_4)_2S_2O_8$, starch | |
| b. KI, $Na_2S_2O_3$, $(NH_4)_2S_2O_8$, starch | |
| c. KCl, $(NH_4)_2S_2O_8$, starch | |

Try to verify your hypothesis by experimenting with these solutions. State clearly the experiment you performed and your conclusions.

Briefly summarize what you think are the roles of KI, KCl, $(NH_4)_2S_2O_8$, $Na_2S_2O_3$, and starch. Show your conclusions to your instructor to have the validity of your observations and hypotheses checked.

| Solution | Role |
|---|---|
| a. KI | |
| b. KCl | |
| c. $(NH_4)_2S_2O_8$ | |
| d. $Na_2S_2O_3$ | |
| e. starch | |

4. Now for the full clock reaction. Make up two solutions as described below.

Solution I: Measure 8 drops of 0.20M KI, 4 drops of 0. 005M $Na_2S_2O_3$, and 1 drop of starch.

Solution II: Measure 8 drops of 0.10M $(NH_4)_2S_2O_8$. Record the room temperature.

Temperature: _____

Quickly mix solution I and II recording the time of mixing.

When the solution suddenly turns blue record the time. Repeat this procedure until you get a constant time interval.

Time of reaction: _____

5. Refer to your results in Step 3 and verify that they are consistent with results in Step 4; if not, repeat any part about which you are unsure. Summarize what you think is occurring.

6. Concentration Effect. The so-called "Law of Mass Action" suggests that the rate of a chemical reaction is affected by changes in the concentration of the reactants. Hypothesize what you think the results would be if you were to decrease by one-half the amounts of KI, $(NH_4)_2S_2O_8$, $Na_2S_2O_3$, and starch?

| | **Solution** | **Predicted Rate** |
|---|---|---|
| a. | KI | _____ |
| b. | $(NH_4)_2S_2O_8$ | _____ |
| c. | $Na_2S_2O_3$ | _____ |
| d. | starch | _____ |

Now test your hypotheses by designing an experiment. Remember that **you must change only one variable at a time.** If, for example, 10 drops of KI are used instead of 20 drops, the total volume will be less and hence all concentrations would be altered. To remedy this you must replace the missing 10 drops. If this is done with 10 drops of deionized water, the correct volume of solution would be obtained.

Clearly state your experiment and record your observations.

| Solution | Time of reaction | Observation |
|---|---|---|
| a | _____ | _____ |
| b | _____ | _____ |
| c | _____ | _____ |
| d | _____ | _____ |
| Step 4 | _____ | |

Explain your results.

7. Temperature Effects. Run the full clock reaction (Step 4) at a different temperature. Record and explain your results. What was the temperature.

Temperature: _____ Time of reaction: _____

## Conclusion

Now that you have been guided through a systematic analysis of chemical reactions, from simple binary combinations to complex processes, you should be able to suggest the actual reactions taking place in the "clock" reaction. In addition, you should be able to discuss how changes in concentration and temperature affect reaction rates. These principles are important and will, therefore, be used throughout this course. The key point when designing your own experiment, as you will do in most of our labs, is to change only one variable at a time.

## References:

1. *Hanson, Allen L., J. Chem. Ed., 58, 434 (1981)*

2. *Zumdahl, Steven S., Chemistry, 2 ed, Lexington, MA, D.C. Heath and company, 1989, pp 2-4*

3. *Masterton, William L., Chemistry, Principles and Reactions, Orlando, FL, Saunders College Publishing, 1989.*

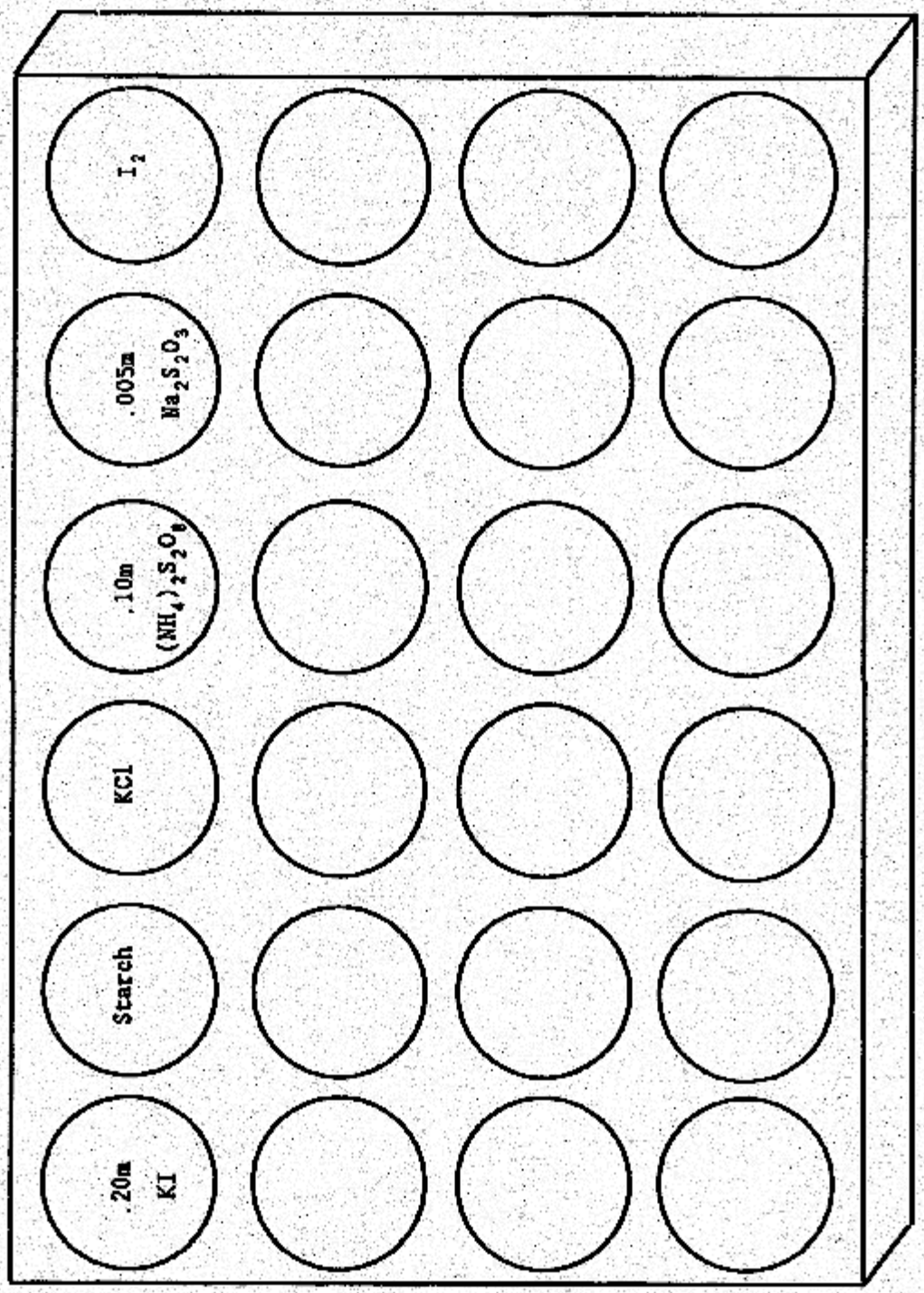
**Experimental Report**

1. Tell which of the following reactions are consistent with your observations and which are not.

| Consistent (Y/N) | |
|---|---|
| _____ | $S_2O_8^{2-} + S_2O_3^{2-} \text{ -------> } SO_4^{2-}$ |
| _____ | $I_2 + S_2O_8^{2-} \text{ --------> } SO_4^{2-}$ |
| _____ | $S_2O_8^{2-} + I^- \text{ --------> } SO_4^{2-} + I_2$ |
| _____ | $I_2 + S_2O_3^{2-} \text{ --------> } I^- + SO_4^{2-}$ |
| _____ | $I^- + S_2O_3^{2-} \text{ --------> } I_2 + SO_4^{2-}$ |
| _____ | $I^- + SO_4^{2-} \text{ --------> } I_2 + S_2O_8^{2-}$ |
| _____ | $Cl^- + S_2O_8^{2-} \text{ ------> } Cl_2 + SO_4^{2-}$ |
| _____ | $I_2 + \text{starch } \text{-------> } I_2\text{-starch (blue color)}$ |

2. Devise a reaction scheme (combination of reactions above) which might explain the results in the experiment.

3. How did changes in concentration and changes in temperature affect the rate of reaction?




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# DATA ANALYSIS
## Chemistry 131

**INTRODUCTION**

A common tool used to analyze experimental data is a graph. Producing a quality graph (or plot) is not as easy as you might think. Most of you have experience plotting points on a number line. Unfortunately, the proper methods may not have been reinforced or thoroughly developed. This Lab outlines the requirements for creating quality graphs from experimental data, and then discusses some background and tools for manipulating data to produce acceptable graphs.

**THE BASIC REQUIREMENTS OF GRAPHING**

If you examine a piece of quality graph paper, you immediately notice it is divided into several different sized grids. Usually each of these grids is denoted by differing darkness of the grid lines. The purpose of these divisions is to help you graph points accurately, and then extract data from your graph. NEVER use square ruled paper (usually reserved for engineering drawings) to produce graphs. Figure 1 shows the difference between these two types of paper.

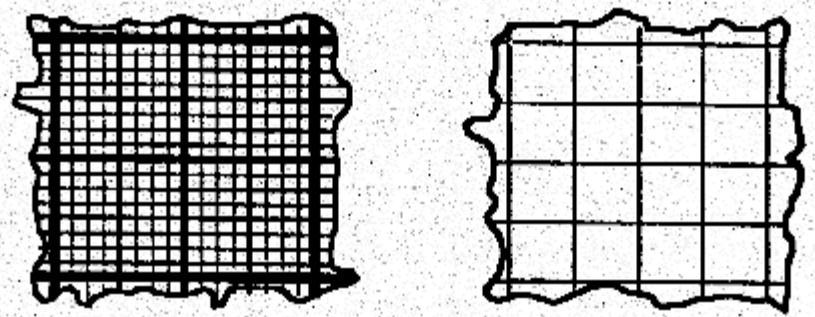



**Figure 1**

**1. PROPERLY SCALED AXES**

The first step to drawing an acceptable graph is to decide how the axes should be aligned on the graph paper. You should arrange the graph so that it fills the majority of the paper (nothing is worse in graphing than a postage stamp sized graph on a sea of empty paper). But which axis should be the "horizontal" axis, and which the "vertical"?

Easy enough. Those in the know have assigned special names to data they wish to graph. All you need to do is follow their lead. Examine your data and decide which set is not affected by the experiment. This is the *independent* data, or the *independent*

*variable*. Usually, this is a quantity that you control or set during the experiment, such as temperature, pressure, volume, or an uncontrollable quantity, like time. The remaining data is what you observed as a result of your experiment. This is the *dependent* variable. **ALWAYS** plot the dependent variable vs. the independent variable. Put another way, the dependent variable is plotted on the Y-axis, while the independent variable is plotted on the X-axis.

Now you are ready to draw the axes on your graph paper. First, each axis should be drawn approximately one inch from the edge of the graph, never on the very edge itself. This allows you to write the scales and titles of each axis on the graph as opposed to writing on the borders. The second requirement is that the X-axis should always be placed so that it runs parallel to the *bottom or right* side of the page, never on the top or left side. Figure 2 shows examples of the correct and incorrect manner of placing the axis on the graph paper.

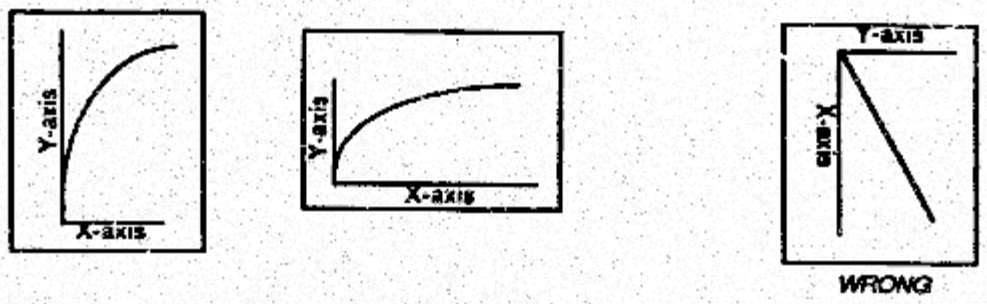



**Figure 2**

In addition, you should scale the axes so that your plot or line will fill most of the graph paper. If you can increase the magnitude of your scale (i.e., spread it out) and still fit the axis on the page, DO IT. Examine your data and identify the range of values you need to plot. For example, your values for the independent variable (X) range from 400 to 800 units, and your graph paper has 25 major divisions along the X-axis you've just drawn. The range of data (400 - 800 + 400) divided by the number of major divisions (25) is 16. Thus, you would "fill" the graph if every major division equalled 16 units. Great, but most graph paper has 10 minor divisions per major division (see Figure 3). Using 16 units for a major division is awkward. Instead, use only 20 major divisions to represent your range of 400 units. Now, the major divisions represent 20 units each, and you've filled your graph paper with graph!

Two other tools for filling the page are: 1) Do not use zero as the origin if your data doesn't go to zero (as in our above example), or to rotate the page and place the X-axis along the long side of the paper.

Finally, the minor divisions of your axis should indicate the same number of significant figures as your data contains. If your measured value is 1.93, you have to be able to read 1.93 on your graph.

**2. AXES LABELS**

Both axes must be labeled. The label should be a one or two word description of the quantity represented by the axis, and the units of the measured quantity. As an example, assume you have measured pressure as a function of time. The Y-axis would be labeled "Pressure (torr)"(the dependent variable) and the X-axis labeled "Time(seconds)"(the independent variable).

When choosing the labels, it is important to remember the scaling chosen when you drew the axes. Consider the following set of data:

| TIME (seconds) | PRESSURE (torr) |
|---|---|
| 0 | 750 |
| 10 | 870 |
| 50 | 930 |
| 100 | 1330 |
| 150 | 2010 |

It may be difficult, and it would be inconvenient, to write the number 2010 on the Y-axis. Instead, change the number to $2.010 \times 10^3$ and label the axis with single whole numbers. This has been done in Figure 3. Each whole number on the axis actually represents a much larger number. You have now chosen a different way to represent the scale on the graph.

Note that in order to plot the data as a number less than ten, we multiplied it by $10^{-3}$. Thus, any number we read from the plot is actually $Y \times 10^{-3} = Y'$, where Y' is the value read from the graph. The new label would be "Pressure x $10^{-3}$ (torr)", indicating that the actual value of pressure was multiplied by $10^{-3}$ before being plotted.

**3. PLOTTING POINTS**

Now that you have correctly drawn and labeled each axis, you are ready to plot the data. Always use a sharp pencil or fine point writing instrument to place the data points on the graph. Around each point draw a small geometric figure such as a circle, square, rectangle, triangle, etc. It is best to use a stencil to do this. These geometric figures will help to correlate multiple sets of data on the same graph into groups, as well as help you locate the data points. Each set of data now has its own geometric figure, which you should list in a legend under the title block of the graph.

**4. THE CURVE (OR LINE)**

Plotted data is of little use if some trend or relationship cannot be established. To see a trend in the data clearly, we draw a curve (which may be a straight line) through the data. There are two general ways for drawing this curve: the "eye-ball" method, and the mathematical fit method. Let's first discuss the "eye-ball" method.

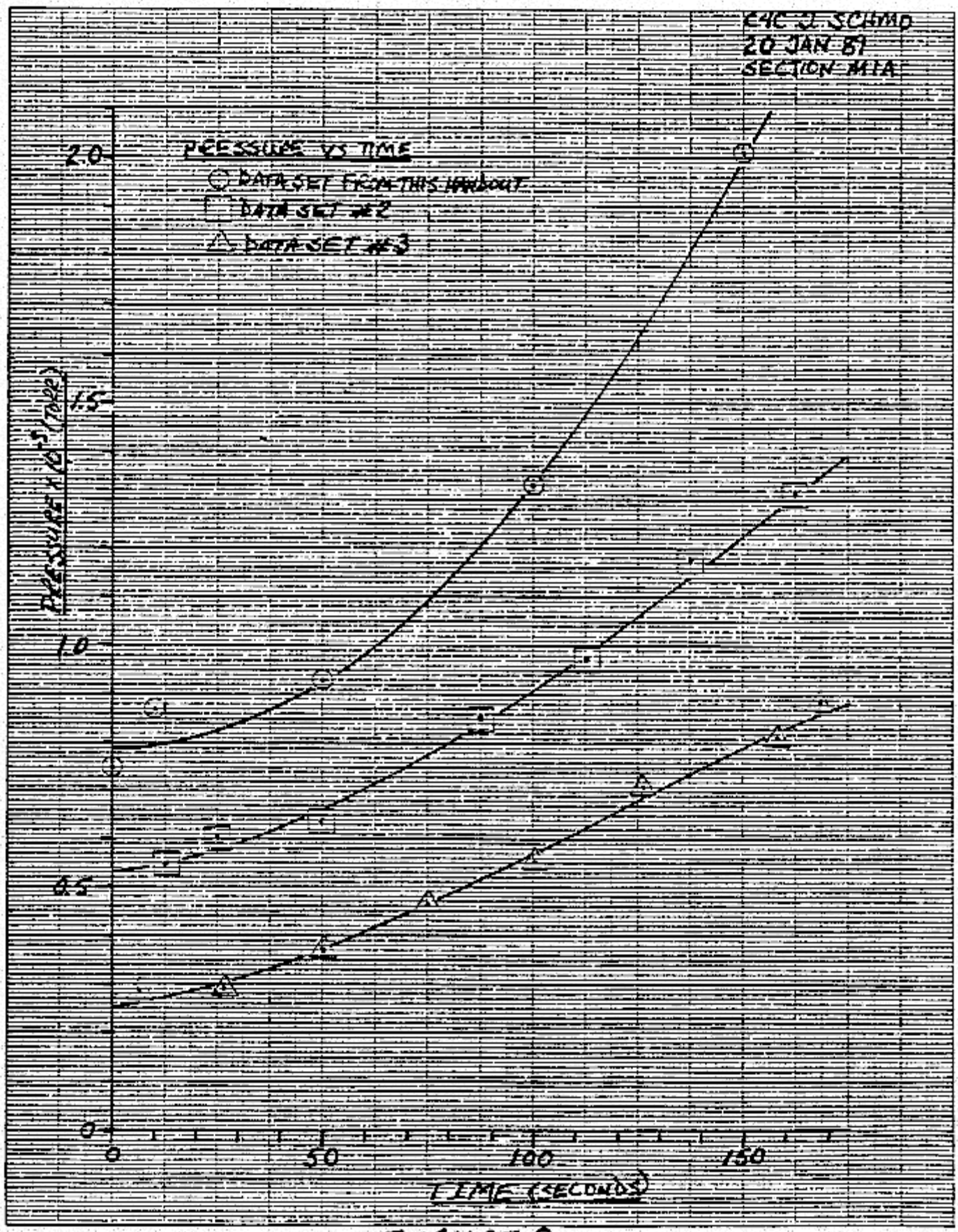



FIGURE 3
GRAPHING 4

SQUARE 10 X 10 TO THE CENTIMETER A3-8014 -8
GRAPHIC CONTROLS CORPORATION
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Eye-ball Method

NEVER play "connect the dots" with your data. The object is to draw a smooth curve which best represents your data. Two types of tools are available to help you do this: rulers and French Curves. Examine your data and determine (by "eye-ball") if a straight line or a curved line best matches your data.

If a straight line is required, then the ruler is the tool you need.

If you believe a curved line is the answer, then a French Curve will best suit your needs. Choose the curve that allows you to draw the best fit to your data (it is not uncommon to use two or three different French Curves to construct a single curved line). Align the curve you chose to three data points at a time. It is not necessary that the curve pass through each point, you might need to select an "average" position with respect to several data points. This requires that even though you are only matching three points, you must keep in mind the entire set of data while constructing your graph.

If your data doesn't appear to be either a straight line or a curve, of if you're just not sure, then the next method of fitting your data to a curve should be used. In this method we use a mathematical model as the tool to fit the data.

Mathematical Fit Method

There are many methods to mathematically manipulate experimental data. You may have heard of some of these manipulations as least squares, power curve, linear regression, etc. Any of these are very useful tools, though some are much more complicated than others. An excellent source book is Curve Fitting for Programmable Calculators by William M. Kolg. It contains in-depth discussions of several curve fitting tools, and programs for programmable calculators (or personal computers) to do the curve fitting analysis. I will limit this discussion to the most common form, linear regression analysis.

Linear regression analysis, or curve fit, is used when and only when you are reasonably sure your data represents a straight line of the form $y = mx + b$. Many calculators have a linear regression analysis function built in, or may be programmed to perform the analysis using three mathematical formulas. These three formula are used to determine the slope (m), the y-intercept (b), and the "goodness" of the fit ($r^2$). The equations are listed below if you do not have a calculator to do this for you.

$$m = \frac{\Sigma x_i y_i - \frac{\Sigma x_i \Sigma y_i}{n}}{\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}} \qquad b = \frac{(\Sigma y_i - m\Sigma x_i)}{n}$$

$$r^2 = \frac{\left[\Sigma x_i y_i - \frac{\Sigma x_i \Sigma y_i}{n}\right]^2}{\left[\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}\right]\left[\Sigma y_i^2 - \frac{(\Sigma y_i)^2}{n}\right]}$$

The coefficient of fit, $r^2$, is an indication of how well the data fits a linear graph. Generally, the closer $r^2$ is to 1.00, the better the fit of the data to a straight line. In each of the equations n is the number of data points. Recall that $\Sigma$ is the summation symbol. For X = 1,2, and 3; $\Sigma x_i$ means 1 + 2 + 3, or 6. Be careful to note the difference between $\Sigma x_i^2$ and $(\Sigma x_i)^2$. The first means $1^2 + 2^2 + 3^2 = 14$, while the second would mean $(1 + 2 + 3)^2 = 36$.

If your data does not represent a straight line, then you should resort to the other tools available. These include the least squares analysis, logarithmic, power, or polynomial curve fitting models in order to obtain a mathematical relationship for the data. Detailed information on these tools may be found in many textbooks on statistics, as well as the source book I've already mentioned by W.M. Kolg.

Computer Based Spreadsheets

Computer based spreadsheets make the handling and manipulation of large amounts of data a breeze. The most useful ones include a graphing package that will take any data you input, and produce acceptable graphs. During the laboratory period you will make several plots and perform curve fitting with the aid of a spreadsheet.

**5. TITLE BLOCK**

The title block contains at least two parts: the graph title and data points legend (as seen in Figure 3). Make your title a short, clear description of the graph's contents. This makes it easier to reference in a text, as well as provide the viewer a starting knowledge of the data portrayed. Always place the title block near the top of your graph (remember, the X-axis is at the bottom).

**PROCEDURE**

1. Using a spreadsheet graph the following data set. If the plot appears linear, find the slope and intercept by curve fitting and report the equation of the line in the form y = mx + b. Make sure you obtain a printout of your data, graph, and curve fit.

| dependent variable | independent variable |
|---|---|
| 1 | 0 |
| 7 | 2 |
| 13 | 4 |
| 22 | 7 |
| 31 | 10 |
| 34 | 11 |
| 43 | 14 |
| 46 | 15 |
| 52 | 17 |
| 55 | 18 |

2. Now plot the following data on a separate graph.

| dependent variable | independent variable |
|---|---|
| 5 | 1 |
| 8 | 2 |
| 13 | 3 |
| 40 | 6 |
| 68 | 8 |
| 85 | 9 |
| 125 | 11 |
| 229 | 15 |

Does the plot appear linear? _____

This data can be fit to the general form $y = x^n + b$. In order to obtain a linear graph you must take the logarithm of the data points to make the general form $\log y = n \log x + \log b$.

Use the spreadsheet to take the logarithm of your data points and replot the data. Now use the curve fitting routine to find the slope and intercept of $\log y = n \log x + \log b$. Report the equation for the data in the form $y = x^n + b$. Make sure you obtain your printouts.

3. We'll now look at some typical data for a lab you will perform later this semester - the determination of an equilibrium constant, $K_c$. Thermodynamic information ($\Delta H$ and $\Delta S$) can be found by measuring $K_c$ at a known temperature and using the equation

$$\ln K_c = -\frac{\Delta H}{R}\left[\frac{1}{T}\right] + \frac{\Delta S}{R}$$

R is the gas constant, 8.31 J/mol K and T is temperature in Kelvin.

Make an appropriate graph for the following data and find $\Delta H$ and $\Delta S$.

| $K_c$ | T (°C) |
|---|---|
| 131 | 21 |
| 115 | 1 |
| 182 | 37 |

**PRELAB GRAPHING ASSIGNMENT**

For the following sets of data, produce two plots on the same piece of graph paper plotting volume as the dependent variable and temperature as the independent variable. Be sure to draw the appropriate "smooth curve" through each set of data. If the plot appears to be linear, perform a linear regression analysis by hand using the equations on p.5 and provide the mathematical relationship for that set of data.

Data Set #1

| Volume (ml) | Temp (K) |
|---|---|
| 0.2 | 298 |
| 0.6 | 304 |
| 0.9 | 314 |
| 1.3 | 320 |
| 1.7 | 334 |
| 2.0 | 350 |
| 2.2 | 359 |
| 2.3 | 370 |
| 2.4 | 381 |
| 2.5 | 392 |

Data Set #2

| Volume (ml) | Temp (K) |
|---|---|
| 1.0 | 292 |
| 1.2 | 302 |
| 1.5 | 312 |
| 1.6 | 322 |
| 1.8 | 330 |
| 2.0 | 337 |
| 2.2 | 345 |
| 2.3 | 352 |
| 2.5 | 361 |
| 2.7 | 370 |

# EMISSION SPECTROSCOPY
## Chemistry 131

**THEORY**

Spectroscopy employs radiation to probe the structure of atoms and molecules. There are many types of spectroscopy. Each type probes different limitations. However, visible light spectroscopy is the easiest because we can use our eyes as the detector.

Joseph Fraunhofer, in 1814, was the first to make spectroscopic observations while studying the sun. Later, scientist turned the spectroscope to study flames. In 1885, Balmer recorded a series of visible lines which were emitted from atomic hydrogen. This spectrum was different from other spectra which had been observed. The other spectra contained all of the colors (similar to a rainbow) while the spectrum of atomic hydrogen only contained a few narrow (sharp) lines of only a few colors. Analysis of other elements showed that each type of atom had its own unique spectrum but each consisted only of narrow lines.

In analyzing the visible spectrum of atomic hydrogen, J. R. Rydberg devised a mathematical equation which summarized the observed wavelengths.

$$\frac{1}{\lambda} = R\left[\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right] \qquad (1)$$

In equation (1), $\lambda$ is the wavelength of the observed line (in meters), $n_{final} = 2$, R is a constant which is called the Rydberg constant ($1.09677 \times 10^7\ m^{-1}$), and $n_{initial} = 3,4,5...$where each value of $n_{initial}$ predicted a different $\lambda$.

Other scientists found other series of lines in the IR and UV regions of the spectrum. Each series corresponded to an electron "falling" from a higher energy level down to $n_{final} = 3$ (IR) and $n_{final} = 1$ (UV). Thus, one simplistic equation fully described the complete spectrum for atomic hydrogen. But what did this say about what the hydrogen atom was doing?

Niels Bohr hit upon the model for hydrogen which successfully accounted for the known experimental results. In analyzing the visible spectrum of atomic hydrogen in 1913, Bohr found that an energy of an electron in a given orbit is

$$E = \frac{-B}{n^2} \quad (n = 1,2,3...) \qquad (2)$$

where B is a constant equal to $-2.179 \times 10^{-18}$ J/photon. To find the energy of a transition of an electron going from an initial higher energy level to a final lower energy level, equation 2 is used. This results in

$$\Delta E = E_{initial} - E_{final} \tag{3}$$

$$\Delta E = -B \left[ \frac{1}{n_{initial}^2} - \frac{1}{n_{final}^2} \right] \tag{4}$$

rearranging, substituting in the constant B, and dropping the $\Delta$, equation 4 becomes

$$E = 2.179 \times 10^{-18} \left[ \frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2} \right] \tag{5}$$

To find E in the common unit of kilojoules per mole, equation 5 becomes.

$$E = 2.179 \times 10^{-18} \frac{J}{Photon} \frac{6.022 \times 10^{23} photons}{mole} \times \frac{1kJ}{10^3 J} \left[ \frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2} \right]$$

$$E = 1312 \left[ \frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2} \right] \frac{kJ}{mole} \tag{6}$$

Once we know the energy of a photon, we can readily calculate the wavelength of the photon using the relationship

$$E = \frac{hc}{\lambda} \tag{7}$$

where h is Planck's constant ($h = 6.63 \times 10^{-34}$ J·sec) and c is the speed of light ($2.998 \times 10^8 \frac{m}{sec}$). The frequency ($\nu$) can be determined by making use of the relationships between the speed of light, wavelength and frequency.

$$c = \lambda \nu \tag{8}$$

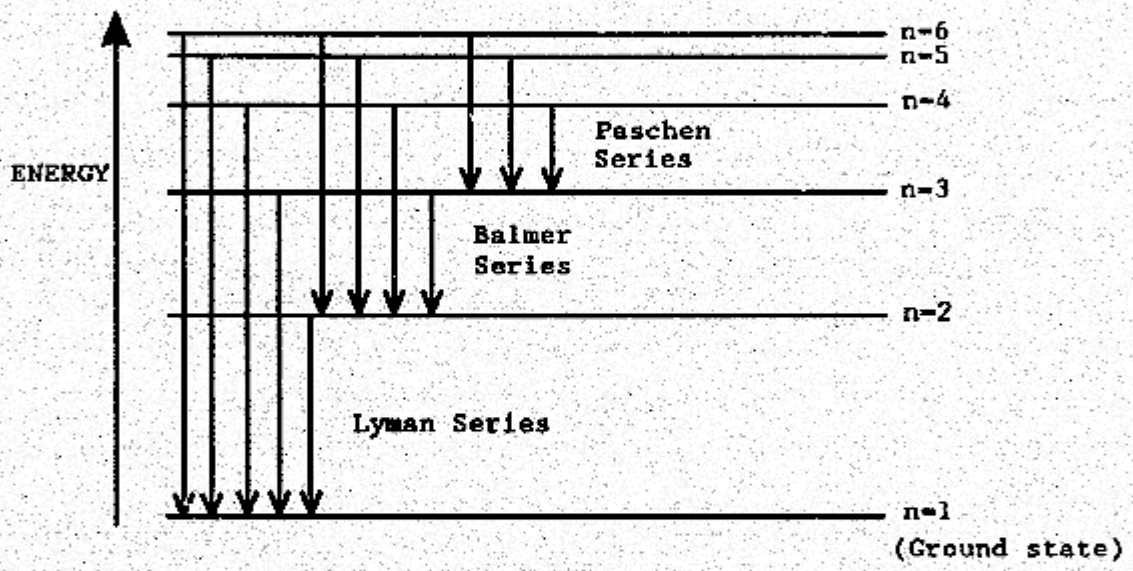
and thus,

$$E = h\nu \tag{9}$$

In summary, the emission levels of hydrogen are the result of an excited electron from a higher energy level "relaxing" to a lower energy level. The energy is released in the form of electromagnetic radiation. The following diagram shows some of the energy levels and transitions of the hydrogen atom. Lines in the Balmer series (visible light) arise from transitions from upper energy levels (n>2) to n=2 level. The Lyman series lines (UV) result from transitions from higher energy levels (n>1) to n = 1. The Paschen series lines (IR) are the result of transitions from higher energy levels (n>3) to n=3 level.

Note that this concept worked well for the hydrogen atom, but not for any other atom at all!!

**Energy Transition of Hydrogen Atom**




**Spectroscopes**

You have already had experience with various spectroscopic devices. Your experiences probably include rainbows and prisms. From these you should know the names we associate with various regions of the visible spectrum. You should also recognize that certain procedures are required for proper operation. Obviously the proper viewing method for a rainbow is different from the viewing method for a prism.

The spectroscope requires a minimum of two components: a dispersive medium to break the light apart by wavelength (or frequency) and a measuring device. Our spectroscope uses a diffraction grating which is a piece of clear plastic with thousands of microscopic scratches. Our measuring device is a glass rod.

Both of these are mounted on a cardboard box which allows for proper control and reliable measurements.

## EXPERIMENTAL

### Purpose

1) Gain an understanding of instruments by operating a spectroscope.

2) Understand the operating parameters of a visible light spectroscope.

3) Observe, record and analyze atomic spectra.

### Procedure

Your spectroscope box is pre-assembled. The remaining tasks are to attach the diffraction grating and install the glass measuring rod.

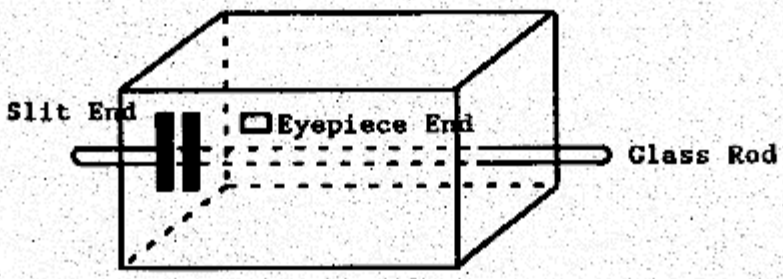



**Figure 1. Spectroscope**

If instructed, remove and discard the small piece of transparent plastic taped over the "eyepiece" opening (see Figure 1) of your spectroscope. When your instructor gives you a new piece of grating, handle it carefully. Touch only the corners. Touching the middle allows oil from your fingers to cover the tiny groves.

Attach the grating only <u>after</u> performing the following procedure. Touching only the corners of the grating, hold the grating over the "eyepiece" opening. Now point the slit opening toward a fluorescent light and look through the grating into the "eyepiece" opening. If your grating is positioned correctly you should see the visible spectrum spread out to the left or right side of the slit. If you don't see the spectrum, rotate your grating 1/4 turn (90°) and look again. When you see the spectrum spread-out as shown in Figure 2, carefully tape the corners of the grating in-place. If you still don't see the spectrum after rotating the diffraction grating, get help from your instructor.

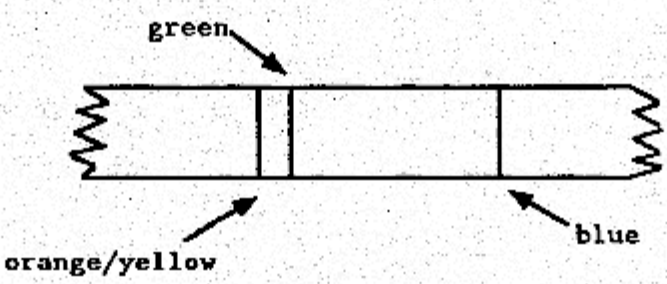



**Figure 2. Fluorescent Light, Mercury Spectrum**

Next obtain a glass rod from your instructor. The glass rod should have a narrow scratch near the middle. If you cannot find the scratch ask your instructor for help in creating your own scratch. Place the glass rod through the two holes in the side of the spectroscope box near the slit end. Look through the grating and verify the scratch on the glass rod is visible near the spectrum and that you can move the scratch all the way from the red-end to the blue-end of the spectrum. Now you're ready to use your spectroscope.

**Adjusting the Slit**

Look closely at the spectrum your spectroscope produces from a fluorescent lamp. In the fluorescent lamp, mercury atoms are excited by the flow of electricity through the lamp. Excited mercury atoms emit photons of light of various energies (or wavelengths) including UV (ultraviolet). A mixture of powdered chemicals on the inside surface of the lamp absorbs this light and emits many different wavelengths. The many wavelengths, combined, produce white light - the rainbow like spectrum in your spectroscope. But included in the spectrum are three of the original mercury lines shining slightly brighter than the rest, see Figure 3.

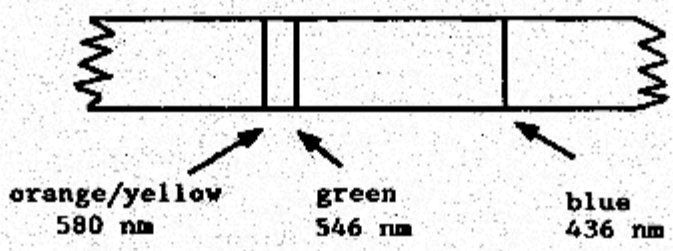



**Figure 3. Mercury Calibration Spectrum**

You will use the mercury lines to observe the effect of changing the width of the slit opening of your spectroscope. Start

by removing the two pieces of black electrical tape from the slit opening. What happened to the three mercury lines?

Now, replace the electrical tape but make the slit as narrow as possible. Describe the appearance of the three mercury lines.

Now adjust the width of the slit for the best combination of sharpness and brightness of the mercury lines. Measure and record the width here.

**Calibration**

The calibration of your spectroscope simply means measuring how well your spectroscope separates wavelengths. This is done by measuring the distance between known emission lines. A convenient source of emission lines is the mercury fluorescent lamp. Look through the eyepiece of your spectroscope and find the three mercury

lines. Move the glass rod so that the scratch is aligned with one of the emission lines. Now measure the length of the remaining glass rod on one side of the box. Align the scratch on the next emission line. Again, measure the length of the glass rod. (Be sure to measure from the same side of the box). Repeat this procedure for the final line. Record the data in the following box.

| Hg Emission Line | Wavelength (nn) | Glass Rod Distance (mm) |
|---|---|---|
| blue | 436 | |
| green | 546 | |
| orange/yellow | 580 | |

The calibration curve is determined by plotting glass rod distance (x) versus wavelength (y). This curve will be used to determine the wavelengths of the hydrogen emission lines and others. Figure 4 shows a calibration curve with the hydrogen lines superimposed on the curve.

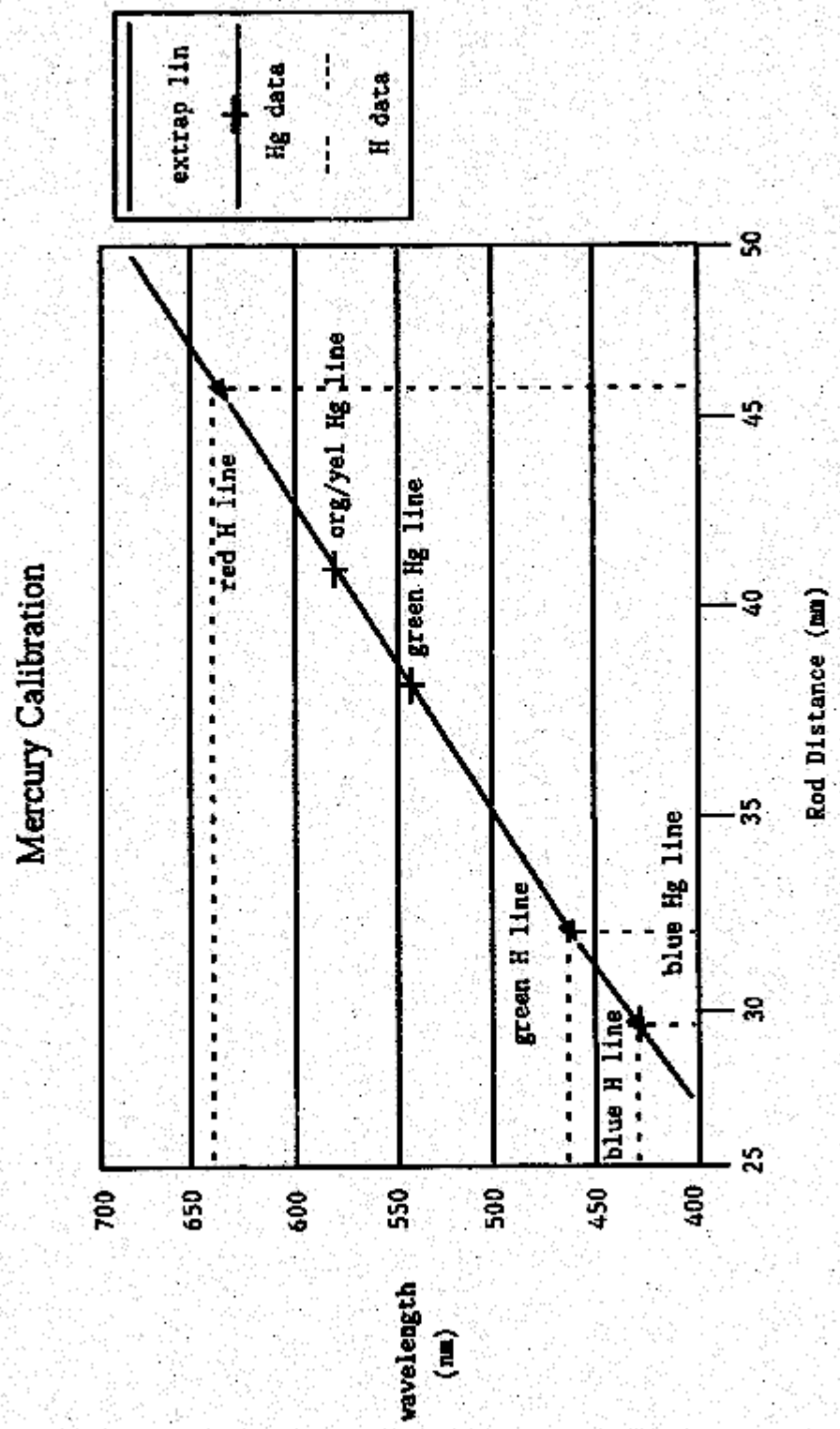

Mercury Calibration
extrap lin
Hg data
H data
red H line
org/yel Hg line
green Hg line
green H line
blue Hg line
blue H line
wavelength (nm)
Rod Distance (mm)
700
650
600
550
500
450
400
25
30
35
40
45
50

Figure 4

4/6

**Hydrogen Atom Emission**

Look at the hydrogen discharge tube with your spectroscope. Describe what you see. (Be sure to include the number of lines, the color of each line, the brightness of each line, the thickness of each line, the rod-position measurement of each line, and any other properties you notice.) A sketch may be helpful. Prepare a table in the space below to collect your data. Leave some space to write-in the actual wavelength which you will interpolate from the calibration graph.

**Helium Atom Emission**

Repeat the same procedure for the helium discharge tube.

**Neon Spectrum**

Repeat for neon. You may not be able to record all of the observed spectrum.

**$SrCl_2$ Flame Spectrum**

Repeat for $SrCl_2$ Flame Spectrum. You may not be able to record all of the observed spectrum.

**KCl Flame Spectrum**

Repeat for KCl Flame Spectrum. You may not be able to record all of the observed spectrum.

**$CaCl_2$ Flame Spectrum**

Repeat for $CaCl_2$ Flame Spectrum. You may not be able to record all of the observed spectrum.

**NaCl Flame Spectrum**

Repeat for NaCl Flame Spectrum. You may not be able to record all of the observed spectrum.

**CONCLUSIONS**

1. Does your calibration line have a positive slope or negative slope? Does it matter? Why?

2. Does the straight calibration line go through all of the data points from the mercury spectrum. If not, why?

3. Calculate the energy associated for each hydrogen emission line. (use equation 7).

4. Calculate the $n_{initial}$ value from equation 1 for each hydrogen spectrum line. Does the lowest $n_{initial}$ value result from the longest wavelength or the shortest wavelength? What is the color of the line associated with the lowest $n_{initial}$ value?

5. Calculate the percent error of your experimentally determined hydrogen emission lines versus the theoretical hydrogen emission lines.

## PRELAB QUESTIONS

Complete the following questions before coming to the lab. Many of the answers will be found in this handout. Your instructor may require you to have this prior to beginning the actual experiment.

1. What wavelength corresponds to the low energy end of the visible spectrum?

2. What wavelength corresponds to the high energy end of the visible spectrum?

3. What is the function of the diffraction grating on the spectroscope?

4. What is the purpose of a calibration graph?

5. The UV emission from what element causes the fluorescent powders in a fluorescent tube to glow?

# CALORIMETRY
# HEAT OF FORMATION OF MAGNESIUM OXIDE
# Chemistry 131

## INTRODUCTION

In this laboratory, we will introduce one of the most often-used techniques in thermochemistry - calorimetry. Although we often think of calorimetry in terms of finding the number of calories in a certain amount of food, calorimetry is valuable to the chemist in measuring basic thermodynamic data. Along with learning calorimetry techniques, you will use the data you collect, along with heats of formation and Hess's law, to determine $\Delta H_f^\circ$ for MgO.

## THEORY

As a quick review, remember that the enthalpy change, $\Delta H$, of a chemical reaction is called the heat of reaction and represents the amount of heat gained or lost as the reaction proceeds from reactants to products. Also, the heat of formation, $\Delta H_f^\circ$, is defined as the amount of heat absorbed when *one* mole of a compound is formed from its elements in their *standard* states. Another important concept is that the enthalpy change of a reaction is independent of its path and depends only on the initial and final states of the reactants and products. This principle is known as Hess's Law and is an example of a state function. Hess's law states that the enthalpy change of a reaction is the same whether it occurs in one step or in many steps.

You will apply Hess's Law in determining $\Delta H_f^\circ$ for the following reaction:

$$Mg_{(s)} + 1/2\ O_{2(g)} \longrightarrow MgO_{(s)} \qquad (1)$$

$$\Delta H_f^\circ = ?$$

This reaction is extremely exothermic and too hard to perform calorimetrically. However, we can find the heat of formation for MgO by combining a series of reactions which are much safer and suitable for a calorimetry experiment. Here is one possible scheme (perhaps you can think of others):

$$Mg_{(s)} + 2H^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_{2(g)} \qquad (2)$$

$$\Delta H = ?$$

$$MgO_{(s)} + 2H^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_2O_{(l)} \qquad (3)$$

$$\Delta H = ?$$

$$H_{2(g)} + 1/2\ O_{2(g)} \longrightarrow H_2O_{(l)} \qquad (4)$$

$$\Delta H_f^\circ = -285.8\ kJ/mole$$

Using Hess' Law, reactions (2), (3), and (4) can be combined to give reaction (1). Work this out for yourself in the box below:

Thus, if the ΔH for reactions (2), (3), and (4) are available, you can find ΔH for reaction (1). You'll use a calorimeter to measure the enthalpy changes for reactions (2) and (3). ΔH for reaction (4) is given so you can find ΔH for reaction (1), the formation of MgO.

Let's examine calorimetry in a bit more detail. First, almost any type of container can be used as a calorimeter, but a well insulated container is best. Why? Because we **must account for all heat that is absorbed or evolved** by the chemical process. Therefore, we want a container from which heat cannot escape to the surroundings. A chemical process occurring in such a system is *adiabatic*; that is, no heat is exchanged between the container and the surroundings. You will use a thermos bottle to achieve adiabatic conditions. (You may ask yourself at this point if the thermos bottle will provide a truly adiabatic environment.)

From here on out we will be talking about adiabatic processes. The important thing to remember when conducting thermochemistry experiments is that you must account for all heat gained or lost during a reaction. For example, if an exothermic reaction occurs in a calorimeter, the heat can basically go two places: (1) the reaction mixture, which can be measured as a temperature rise, and (2) the walls of the calorimeter. Since heat is not transferred between the

calorimeter and the outside, the following must be true:

$$\text{heat from reaction} = \text{heat absorbed by calorimeter} + \text{heat absorbed by reaction mixture}$$

*or*

$$-q_{rxn} = q_{cal} + q_{liq} \text{ (where q represents heat)} \quad (5)$$

Thus the heat lost by the chemical reaction is exactly equal to all the heat gained. Why is there a negative sign for $q_{rxn}$?

Now let's examine each of the terms in the equation:

**Heat from Reaction ($q_{rxn}$):** If the heat (q) comes from the enthalpy of a chemical reaction, we can replace q by $n\Delta H$, where n is the number of moles of product and $\Delta H$ is the enthalpy change per mole due to the reaction or phase change. The number of moles of product will be based on the moles of the *limiting* reagent.

**Heat Absorbed by the Calorimeter ($q_{cal}$):** For our calorimeter, the heat simply changes the temperature of the calorimeter. We can replace q by $C_c\Delta T$, where $C_c$ is the heat capacity and $\Delta T$ is the temperature change. Note that the heat capacity is the amount of heat required to raise the temperature of the substance by one Kelvin. The units of $C_c$ are usually J/K. Thus we need the heat capacity of the calorimeter, $C_c$, which is specific for each calorimeter. You will find $C_c$ for your calorimeter by performing reaction (7) below for which we have provided $\Delta H_{rxn}$. You will then use equation (6) on the next page to solve for $C_c$.

**Heat Absorbed by Reaction Mixture ($q_{liq}$):** This term is equal to $mC_p\Delta T$. The mass of the solution is m and is equal to the total volume of the solution times the density of solution. We simplify by using density equal to 1.00 g/mL since all the solutions are essentially aqueous. Although for <u>pure</u> water the heat capacity is 4.184 J/(g °C), when ions or molecules are dissolved in it the heat capacity changes. For the NaOH and HCl reaction the heat capacity of the solution, $C_p$, is equal to 4.025 J/(g °C) while for the Mg reactions, $C_p$ equals 3.862 J/(g °C).

Using these expressions for q, equation (5) is rewritten as:

$$-n\Delta H = C_c\Delta T + mC_p\Delta T \qquad (6)$$

where:

n = number of moles of limiting reagent.
$\Delta H$ = heat evolved in the reaction.
$C_c$ = calorimeter constant (specific for your calorimeter).
$\Delta T$ = temperature change resulting from the reaction.
m = mass of the solution.
$C_p$ = specific heat of the solution.

Note that we used $q = mC_p\Delta T$ for the liquid in the calorimeter because we know its exact composition. For the calorimeter itself, however, a heat capacity, $C_c$, was used because the exact composition of the calorimeter is not known.

Now let's apply the theory of calorimetry to your experiment. To find $\Delta H$ for a reaction, all the other values in Equation (6) must be known. The first objective will be to calibrate the calorimeter to find $C_c$. This calibration is accomplished by producing a known quantity of heat from reaction (7) below and measuring $\Delta T$. Since $\Delta H$, the heat capacity, and the quantities of NaOH and HCl are known (assuming that all volumes are additive), the only unknown in equation (6) is $C_c$ which you can now calculate.

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(\ell)} \qquad (7)$$

$$\Delta H_{rxn} = -57.7 \text{ kJ/mole}$$

Once the value of $C_c$ is known, it can be used for reactions (2) and (3) to solve for the unknown $\Delta H_f$.

To use equation (6) you will need $\Delta T$, the temperature change for the reaction mixture and the calorimeter. However, you will not be able to simply measure the maximum temperature because the temperature may never actually reach the maximum. This irregular behavior is due to the calorimeter's inability to absorb heat as quickly as the reaction mixture. You will use a standard graphing technique to extrapolate to the maximum temperature for each of your experiments.

During this experiment you'll measure and record the temperature at given time intervals. You will plot this data on a graph like that shown in Figure 1. Notice the temperature *vs.* time plot is irregular until it stabilizes on a slowly decreasing temperature line. Ideally, you want the maximum temperature that would be produced if the reaction happened instantaneously at the time of mixing (time = 0), not some time later when the reaction mixture and the calorimeter tend to cool slightly. The proper method to obtain $\Delta T$ is depicted in Figure 1. The rate of cooling is used to extrapolate back to what the maximum

temperature should have been. This is the intersection of the extrapolation line with the y-axis (time = 0). The difference between the extrapolated maximum, $T_e$, and the initial temperature, $T_i$, is $\Delta T$.

**EXPERIMENTAL:**

This experiment will be done with a PARTNER.

**A. Prelab Calculations:**

The solutions of HCl and NaOH that you'll use in your reactions must be prepared from our stock solutions. You will make 200 mL of a 1.00 M HCl solution from a 6.20 M stock solution. You'll also make 100 mL of a 1.00 M NaOH solution from a 3.10 M stock solution. Prior to lab, calculate the volume of each stock solution and $H_2O$ that you'll mix together to make your solutions.

To make 100 mL of 1.00 M HCl, start with _____ mL of 6.20 M HCl and dilute it in a volumetric flask to a final volume of _____ mL.

You will need to repeat this twice since you will need a total of 200 mL 1.00 M HCl.

To make 100 mL of 1.00 M NaOH, start with _____ mL of 3.10 M NaOH and dilute it in a volumetric flask to a final volume of _____ mL.

1. **Prepare stock solutions:** (One partner should do this while the other partner is weighing the solid chemicals.) Use two clean 100 mL beakers to get stock solutions from the side shelf and mix them with the calculated amounts of water in 250 mL beakers. *Record* accurately the exact molarity of HCl and NaOH as labeled on the containers and the exact volumes of HCl, NaOH, and water used. You'll need this data to calculate exact concentrations of your solutions.

2. **Weigh solid chemicals:** (The other partner should do this while the first partner is preparing the solutions.) The Mettler balances are delicate instruments. Do not spill any chemicals on the balance. If you do spill chemicals, clean them up immediately. To weigh a chemical, place a clean, small piece of paper on the top of the balance. Press the **TARE** button to **ZERO** the balance. Add the solid slowly onto the paper until the proper mass has been weighed.

a. Weigh 0.20 to 0.30 g of Mg turnings to the nearest milligram on the Mettler balance. Record the exact mass of Mg used.

b. Separately weigh 0.50 to 0.60 g MgO weighed to the nearest milligram. Again, record the exact mass.

## B. Calorimeter Calibration (Finding $C_c$):

> **WARNING:** The precision thermometers and thermos bottles are expensive. Treat them with care. If you break a thermometer, tell the lab instructor *immediately* so the mercury spill can be cleaned up. Also, HCl stains bench tops; clean up spills immediately!

1. Record your calorimeter number and insure the calorimeter and thermometer are clean and have been rinsed with de-ionized water.

2. Using a 50 mL graduated cylinder, measure 50 mL of your 1 M HCl solution. Pour the HCl into the calorimeter. Insert the thermometer assembly and record the temperature when it stabilizes (This should take less than 3 minutes). Measure all temperatures to the nearest 0.05°C with the aid of a magnifying glass.

3. Now rinse the graduated cylinder successively with tap water, de-ionized water, and 5 mL of 1 M NaOH solution. Measure 50 mL of your 1 M NaOH solution in the graduated cylinder and pour into a small, clean, dry beaker. Record the stabilized temperature of the NaOH solution. The average between this temperature and the HCl temperature in the calorimeter previously recorded is to be used as your initial temperature ($T_i$).

4. Noting the time, pour the NaOH into the calorimeter. Immediately insert the thermometer assembly and gently swirl the reactants. Record the temperatures to the nearest 0.05°C at half-minute intervals until a maximum is reached; then record at one minute intervals until enough data is obtained for an extrapolation (5 to 10 minutes). Gently swirl the reaction mixture between each reading.

| Time | Temperature °C | Time | Temperature |
|---|---|---|---|
| 0 | | 330 | |
| 30 | | 360 | |
| 60 | | 390 | |
| 90 | | 420 | |
| 120 | | 450 | |
| 150 | | 480 | |
| 180 | | 510 | |
| 210 | | 540 | |
| 240 | | 570 | |
| 270 | | 600 | |
| 300 | | | |

## C. Heat of Reaction of Mg and HCl:

1. Clean and dry your calorimeter and add to it 50 mL of your 1 M HCl solution and 50 mL of de-ionized water. Record the stabilized temperature ($T_1$).

2. Noting the time (t = 0), drop the Mg into the calorimeter. Immediately put the thermometer assembly in place and swirl gently. Record temperatures at half-minute intervals until a maximum is reached; then record at one minute intervals for at least five minutes. Gently swirl the reaction mixture between each reading.

| Time | Temperature |
|---|---|
| 0 | |
| 30 | |
| 60 | |
| 90 | |
| 120 | |
| 150 | |
| 180 | |
| 210 | |
| 240 | |
| 270 | |
| 300 | |
| 330 | |
| 360 | |
| 390 | |
| 420 | |
| 450 | |

**D. Heat of Reaction of MgO and HCl:**

1. Using the same calorimeter, repeat the procedure used in Part C using MgO in place of Mg. (Note: You must swirl the calorimeter vigorously while reacting MgO and HCl since the MgO tends to form lumps at the bottom of the calorimeter and fails to dissolve. This could cause considerable error.) Hold the thermometer assembly in the calorimeter so it will not rattle while swirling. Record temperatures at half-minute intervals until a maximum is reached; then record at one minute intervals for five minutes. Gently swirl the reaction mixture between each reading. When it appears that temperature changes have ceased, quickly look into the calorimeter. If a white solid remains at the bottom, the calorimeter must be swirled more vigorously until all of the MgO has dissolved.

| Time | Temperature |
|---|---|
| 0 | |
| 30 | |
| 60 | |
| 90 | |
| 120 | |
| 150 | |
| 180 | |
| 210 | |
| 240 | |
| 270 | |
| 300 | |
| 330 | |
| 360 | |
| 390 | |
| 420 | |
| 450 | |

ENTHALPY 10

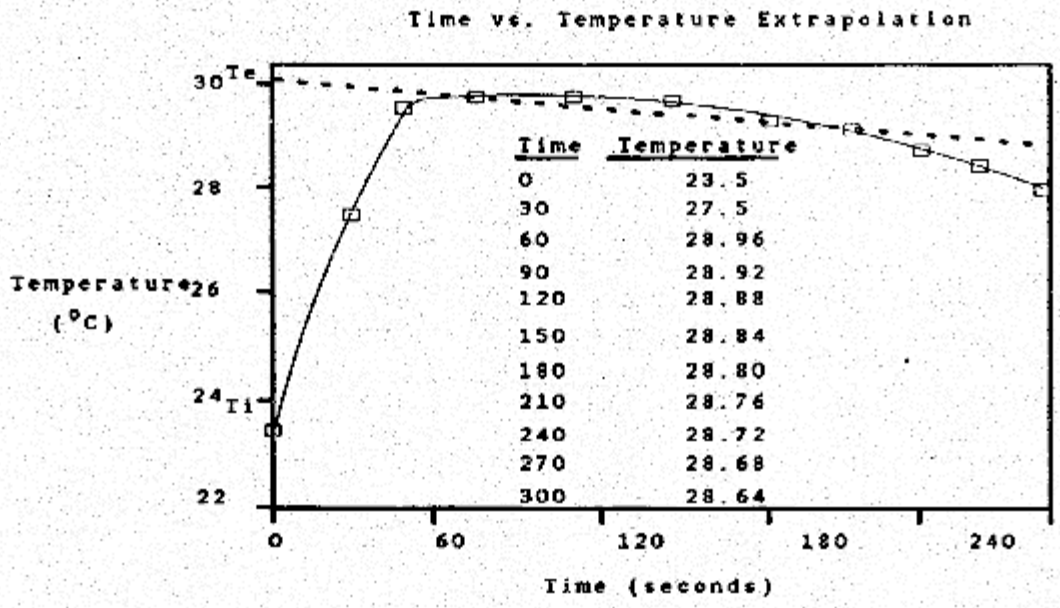

Time vs. Temperature Extrapolation
Temperature (°C)
30
28
26
24
22
Te
Ti
0
60
120
180
240
Time (seconds)
Time Temperature
0 23.5
30 27.5
60 28.96
90 28.92
120 28.88
150 28.84
180 28.80
210 28.76
240 28.72
270 28.68
300 28.64

**FIGURE 1**

**RESULTS**

**A. Calculations:**

1. Record all volumes and weights of chemicals used and show calculations for all values necessary to report the required values. Be sure to include:

a. Dilution of all stock solutions.

b. For each reaction:

Moles of reactants and products.
Limiting "Reactant" calculations

c. Calorimeter constant.

d. $\Delta H$ for reactions 2 and 3 and $\Delta H_f^\circ$ of MgO.

**B. Graphs:**

1. In this experiment, a good graph is critical to finding the correct temperature changes for each reaction and is an integral part of your calculations. Without it, your calculations are of no value. Refer to your "Data Analysis" handout if you've forgotten the proper way to draw a graph. Label $T_i$ and $T_e$ on the temperature axis and show your extrapolation to find $\Delta T$. You will probably need to draw each graph on a separate sheet of graph paper.

a. After plotting your data points of temperature vs. time, draw a smooth curve through these points. Your initial point at time = 0 will have the initial temperature ($T_i$) of the solution prior to mixing (refer to Figure 1). Draw a straight line from your "stabilized" data (data recorded over the one minute intervals) back to the Temperature axis. This is your extrapolation. The extrapolated temperature, $T_e$, is the temperature where this extrapolation line intersects the y-axis.

b. Use $T_e$ from the extrapolation line, and $T_i$ to calculate $\Delta T$.

**CONCLUSIONS:**

A. Why was it necessary to use adiabatic conditions?

B. Is the formation of MgO exothermic or endothermic?

C. How does your value of $\Delta H_f^\circ$ compare with the actual literature value? Calculate the percent difference between your value and the actual literature value. This is:

$$\% \text{ Difference} = \frac{(\text{experimental value}) - (\text{actual value})}{(\text{actual value})} \times 100$$

Comment on possible sources of error.

# DATA FROM ANALYSIS OF PRESENT AND FUTURE ENERGY RESOURCES

by

Major Steven E. Dunlap
Department of Chemistry
United States Air Force Academy

## CURRENT MAJOR ENERGY SOURCES

| | |
|---|---|
| Oil | 43% |
| Coal | 23% |
| Natural Gas | 22% |
| Nuclear | 6% |

## OIL RESOURCES

### WORLD

| | |
|---|---|
| 600 | billion barrels of known reserves |
| 525 | billion barrels of estimated undicovered recoverable |
| 21.7 | billion barrels per year current consumption |
| 27 | years remain of known reserves at current consumption |

### UNITED STATES

| | |
|---|---|
| 24.6 | billion barrels of known reserves (4% of world's, had 15% initially) |
| 5.9 | billion barrels per year current consumption |
| 3.16 | billion barrels per year current production |
| 7.8 | years remain of known reserves at current production |

### UNITED STATES IMPORTS

2.74 billion barrels per year (46.4%)

| | | |
|---|---|---|
| 19% | Canada | 12.8 years remain at current production |
| 10% | U.K. | 9.7 years remain at current production |
| 10% | Mexico | 27.8 years remain at current production |
| 20% | Africa | 29.8 years remain at current production |
| 7% | Venezula | 39.8 years remain at current production |
| 13% | Middle East | |

## COAL RESOURCES

### WORLD

| | |
|---|---|
| 987 | billion tons of known reserves |
| 6-12 | trillion tons of estimated undiscovered recoverable |

### UNITED STATES

| | |
|---|---|
| 283 | billion tons of known reserves (29% of world's) |
| 0.818 | billion tons per year current consumption |
| 346 | years remain of known reserves at current consumption |

## NATURAL GAS RESOURCES

### WORLD

| | |
|---|---|
| 3.6 | quadrillion SCF known reserves |
| 6-12 | quadrillion SCF estimated undiscovered recoverable |
| 59 | trillion SCF per year current consumption |
| 61 | years remain of known reserves at current consumption |

### UNITED STATES

| | |
|---|---|
| 185 | trillion SCF known reserves (5% of world's) |
| 18.2 | trillion SCF withdrawals per year |
| 10.2 | years remain of known reserves at current consump. |

### U.S. IMPORTS

| | |
|---|---|
| 0.75 | trillion SCF per year |

### U.S. EXPORTS

| | |
|---|---|
| 0.06 | trillion SCF per year |

## URANIUM

### WORLD

| | |
|---|---|
| 4.3 | million tons under current mining constraints |
| 26 | million tons technically obtainable |

### UNITED STATES

| | |
|---|---|
| 12-15 | years under current mining practices and planned consumption |
| 50-60 | years using all technically obtainable uranium |

## ESTIMATION OF OIL RESERVES

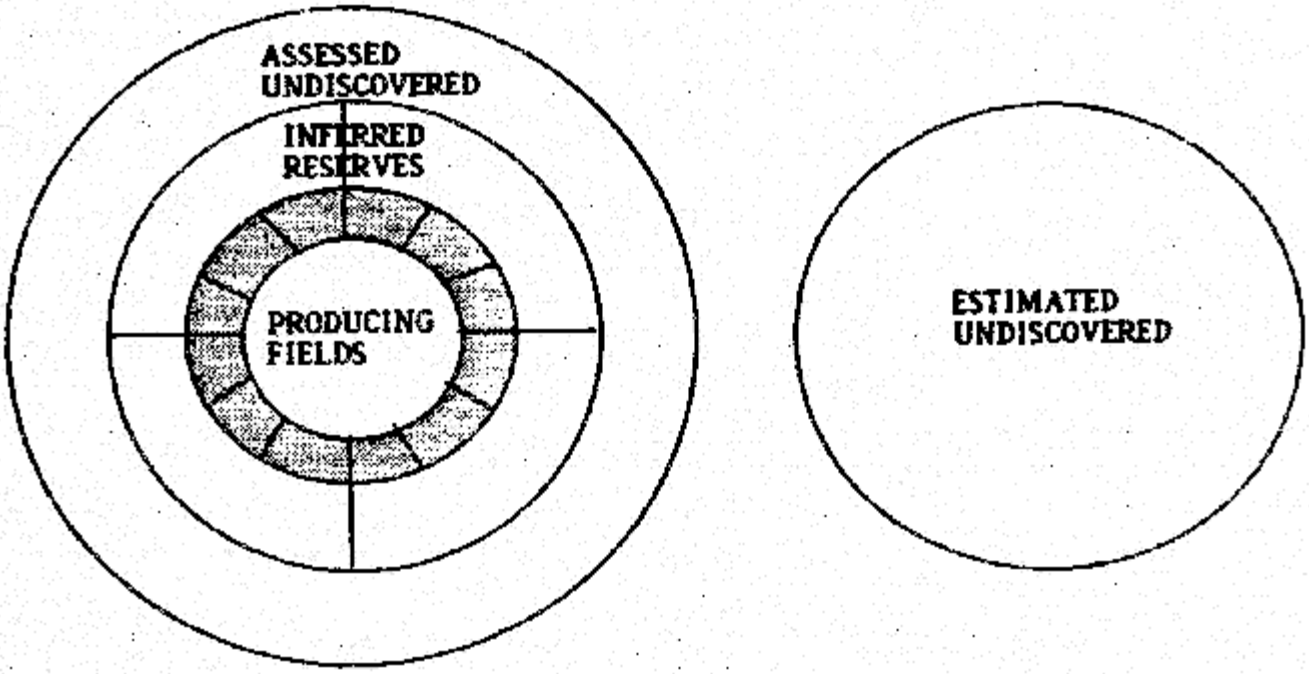
### SEDIMENTARY BASINS

| | |
|---|---|
| 600 | geologically known |
| 160 | productive |
| 240 | non productive |
| 100 | unexplored because of hostile conditions |
| 100 | will probably never be explored because of conditions |

### BREAKDOWN OF RESERVES (BILLIONS OF BARRELS)

| | |
|---|---|
| 532.5 | Cumulative production to date |
| 511.5 | Proved reserves |
| 101.2 | Inferred reserves |
| 513.9 | Assessed undiscovered reserves |
| 294.0 | Estimated undiscovered reserves |

# OIL RESERVES TERMINOLOGY



## EFFECT OF U.S. CONSERVATION

### TRANSPORTATION

0.5-1.2 billion barrels potentially saveable annually
3.16 billion barrels per year current consumption
1.5-4.5 year extension

### RESIDENTIAL USAGE

#### ENERGY USED FOR HEATING

3.6 trillion SCF natural gas per year
0.19 billion barrels of oil per year
0.30 quadrillion BTU of electricity, 14, power plants

#### ENERGY USED FOR AIRCONDITIONING

0.36 quadrillion BTU of electricity, 18 power plants

#### ENERGY USED FOR APPLIANCES

1.53 quadrillion BTU of electricity, 74 power plants

### COMMERCIAL USAGE

2.2 trillion SCF natural gas per year
0.06 billion barrels of oil per year
2.24 quadrillion BTU of electricity, 109 power plants

### POTENTIAL SAVINGS

100 Power plants

## EFFECT OF GROWTH ON WORLD OIL RESERVES

| PERCENT RATE OF INCREASE | | YEARS REMAINING |
|---|---|---|
| 0.00 | | 27 |
| 1.43 | Projected by EIA | 23 |
| 2.66 | Current U.S. | 21 |
| 7.00 | U.S. prior to 1970 | 9 |

## REQUIREMENTS

Total replacement of present major energy sources.

Solve the problem of the heterogeneity of current energy forms.

## NUCLEAR FUEL FROM REPROCESSING OR BREEDER REACTORS

### CAPABILITIES

| | |
|---|---|
| 0.6 | percent of uranium ore's potential energy is harnessed by present once-through reactors |
| 70 | percent of ore's potential energy obtainable using reprocessing or breeders |
| 1000s | of years fuel possible at current rate of use and with present mining practices |
| 100,000s | years if lower grade ur[illegible]n is considered |

### REQUIREMENTS

| | |
|---|---|
| 300 | additional 1000 MW reactors to replace fossil fuel generation |
| 1000 | more 1000 MW reactors to meet total U.S. energy demand |

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### STATUS

France has a 1300 MW breeder on-line.

England should have a large commercial breeder go on-line this year.

Soviets have one breeder under construction and another planned.

Britain has reprocessed from the start.

France has the world's largest reprocessing center at LaHague.

U.S. had an experimental breeder in the 1950s.

U.S. has a 350 MW breeder reactor on order for Clinch River, Tn. (constraction subject to resolution of national policy debate)

U.S. presently has:

| | |
|---|---|
| 100 | operable once-through fission reactors |
| 7 | in startup |
| 19 | construction permits granted |
| 0 | on order |

## PHOTOVOLTAICS

### CAPABILITIES/REQUIREMENTS

Landmass of Maryland and Connecticut to meet current U.S. electricity demand.

Landmass of Nevada or Utah required to meet total U.S. energy demand.

### STATUS

| | |
|---|---|
| 0.1 | MW facility operated by Alabama Power Company |
| 660,000 | MW current U.S. generating capacity |
| $10-30 | cost of cells per watt would increase electricity bills 100 percent. |
| $.1-.30 | cost per watt predicted in 1990s by DOE |
| 10 | year current cell life |
| 20-30 | year cell life necessary to make competitive |

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## BIOMASS

### WOOD

Has eclipsed nuclear power in the United States

75 percent of present forest required to meet current U.S. electricity demand

82 percent of U.S. landmass required to meet total U.S. energy demand

10 years required to properly establish a wood fuel plantation

### FUEL CROPS

17 percent of Brazil's automotive fuel made by fermenting sugar cane

sugar cane doesn't grow appreciably in the U.S.

corn gives half the yield of sugar cane

21 percent of U.S. landmass required to meet automotive fuel requirement

20 percent of U.S. landmass currently cultivated

6 percent of landmass required by some "hopeful" future plants

1200 percent of U.S. landmass required using Calvin's Euphorbia Lathyris

## SYNFUELS
## PAST AND PRESENT PRODUCTION

### OIL FROM SHALE

4400 barrels per day (max), Scotland, 1859-1962

3000 barrels per day (max), Australia, 1862-1952

50 commercial plants, United States, 1859

50,000 barrels per day, China, currently

25,000 barrels per day, Soviets, currently

5,000 barrels per day, U.S., currently

### OIL FROM COAL

50 barrels per day, Scotland, 1850

100,000 barrels per day, Germany, WWII, 1/3 wartime requirement

5,000 barrels per day, SASOL I, 1960-present

58,000 barrels per day, SASOL II, in startup

300 barrels per day, Union Carbide, 1956-1962

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# SYNFUEL RESOURCES

## SHALE

80-600 billion barrels of recoverable shale oil in high grade deposits of Colorado, Utah, and Wyoming
14-102 years at current U.S. consumption

## COAL

0.818 billion tons per year current consumption
10 percent rate of increase in usage proposed by Ford
2.19 billion tons per year in 18 years
meets 3.28 billion barrels of oil import requirement at that time
3.65 billion tons per year in 29 years
meets 5.9 billion barrels of oil total requirement in 29 years
42-57 years remain at this rate of use

## REQUIREMENTS

165 synfuel plants with a capacity of 58,000 barrels per day by 2000

$2-4 billion per plant and 5 years to build each plant

Immediately begin building pioneer commercial scale plants in this country.

## STATUS AND PREDICTIONS

Will not meet the government goal of 0.26 billion barrels per year (4.5%) by 2000 under the current administration.

$88 billion programmed, only $13 billion ever appropriated.

With an all out effort could reach 2-3 billion barrels per year by 2000 and sustain it for 100-150 years.

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## HYDROGEN FOR FUEL

1979 Roger Billings marketed hydrogen powered Dodge Omnis

24 Commercial airline aircraft designs (twice as efficient, 33 percent increase in payload)

1956 USAF flew a B-57 with one engine operating on hydrogen.

1500 tons of nickel to meet 1985 gap in supply and demand for methane

16,000 tons of nickel produced annually by U.S.

To meet U.S. natural gas demand, a severe strain would be placed on domestic nickel production.

## RECOMMENDATIONS

Synfuels should meet import requirements by 2000.

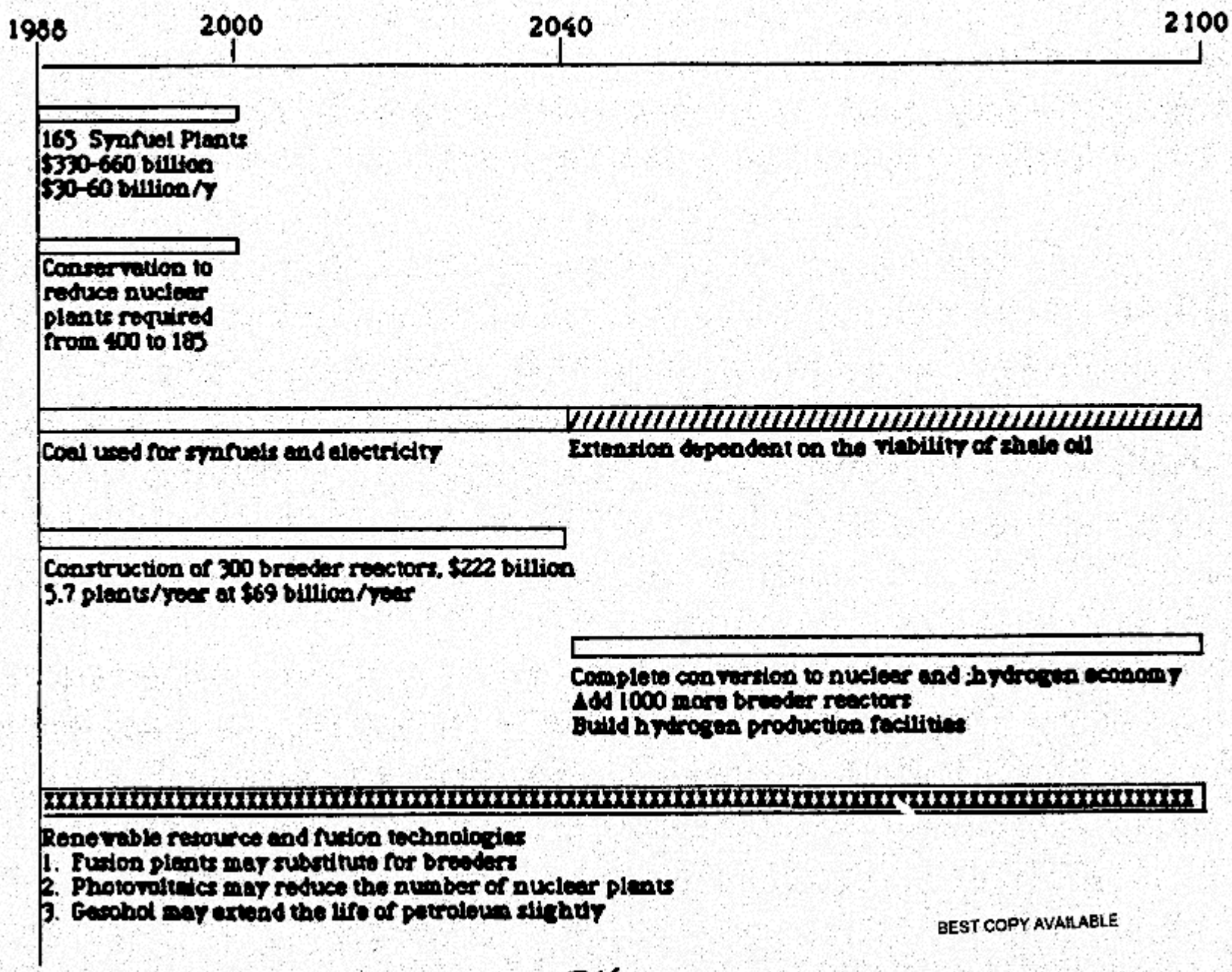
Nuclear fission with reprocessing or breeders must carry electrical load by 2040 and entire energy demand by 2100.

Convert to hydrogen economy between 2040 and 2100 as fossils are depleted.

Renewables, photovoltaics, and nuclear fussion can substitute for some of the above requirements but will not alter the major periods of transition.

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# Recommendati s' Time Line




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# MOLECULAR GEOMETRY AND ELECTRONIC STRUCTURE LABORATORY
## Chemistry 131

**BACKGROUND**

Chemists have techniques by which molecular structures can be determined. Among them are X-ray and neutron diffraction for solids, and microwave rotation spectroscopy and electron diffraction for gases. Other methods used in structural analyses are infrared and raman spectroscopy, nuclear magnetic resonance, and mass spectrometry. Here at the Air Force Academy, the Department of Chemistry and the Frank J. Seiler Research Lab have most of the spectroscopic instrumentation necessary to do these analyses.

**EXPERIMENTAL**

**Procedure**

Although you'll not experimentally determine the 3-D structure of any molecule in this course, you'll become familiar with the many geometric arrangements and molecular structures found in simple molecules. One of the easiest ways to do this is to use models. The kit you purchased at book issue allows you to build a model of each of the geometries found in your text book. Use the various colored balls to represent the different types of atoms in a molecule. There are balls available with two (red), four (blue and black), five (brown), and six holes (gray) to represent the central atoms for all geometries. Try them out. Discover the beauty of three-dimensional geometries.

Attached to this introduction is a prelab worksheet. Fill in each of the columns on it <u>before you come to the lab.</u> Be sure to name each molecule. Also attached is a checklist for doing Lewis structures.

**Equipment**

Bring:

1) The completed prelab worksheet.

2) Your model kit.

3) Your textbook.

to the lab with you.

**A CHECKLIST FOR DRAWING LEWIS STRUCTURES**

1. Determine the central atom. The following are guides:

   a. The least electronegative element is the central atom.

   b. Often the unique atom (only one of it) is the central atom.

   c. Sometimes the formula is written with the central atom in the middle.

2. Arrange the other atoms around the central atom creating a skeleton.

   a. Oxygen rarely bonds to itself except in:

   1) $O_2$ and $O_3$ (ozone).

   2) Peroxides, e.g., $H_2O_2$.

   3) Superoxides, e.g., $NaO_2$.

   b. Fluorine never bonds to more than one atom.

3. Connect all bonded atoms in the skeleton with one bond.

4. Count up the total number of valence electrons. Normally, we consider only the s and p orbital electrons as valence electrons. Don't forget the charge on an ionic species.

5. Subtract the number of electrons already used for the single bonds.

6. Distribute the remaining electrons in pairs around the atoms, trying to satisfy the octet rule. Assign them to the most electronegative atoms first.

7. If you run out of electrons <u>before</u> every deserving atom has an octet of electrons, you need to form double bonds.

8. If you have extra electrons and all of the atoms have an octet, then put the extra electrons on the central atom arranged as pairs. If the central atom is in period 3, 4, 5, or 6 you are allowed to have more than eight electrons around it.

NOTE: This is one of many methods useful when drawing Lewis structures. If you learned a different method, use whichever is easiest for you.

**MOLECULAR GEOMETRY WORK SESSION**

Using your own paper as a work sheet, draw the Lewis structure for each of the molecules listed below. Then tabulate your results in the correct categories on the attached Results Sheets. For molecules that exhibit resonance, draw all the resonance structures.

| | | | | |
|---|---|---|---|---|
| $NH_3$ | $XeF_4$ | $XeF_2$ | $SF_4Cl_2$ | $ClF_3$ |
| HF | $SCl_2$ | $IF_5$ | $NH_4^+$ | $PF_6^-$ |
| $PF_5$ | $BeCl_2$ | $SO_2$ | $SO_3$ | $CH_3Br$ |
| $SO_3^{2-}$ | $PO_4^{3-}$ | HCN | $AlCl_3$ | |

**Work out these additional, more difficult molecules.**

| | | | | |
|---|---|---|---|---|
| $O_3$ | CO | $H_2SO_4$ | $H_3O^+$ | $F_2C_2$ |
| $C_2H_2$ | $CO_2$ | $CO_3^{2-}$ | $H_2N_2$ | |

## MOLECULAR GEOMETRY RESULTS

| | Lewis Structure | -- Number of -- Bonding electron Pairs | -- Number of -- Unshared electron Pairs | Hybridization | Bond Angles | Shape | Polarity |
|---|---|---|---|---|---|---|---|
| $NH_3$ Name: | | | | | | | |
| $XeF_4$ Name: | | | | | | | |
| $XeF_2$ Name: | | | | | | | |
| $SF_4Cl_2$ Name: | | | | | | | |



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## MOLECULAR GEOMETRY RESULTS

| | Lewis Structure | -- Number of -- Bonding electron Pairs | -- Number of -- Unshared electron Pairs | Hybridization | Bond Angles | Shape | Polarity |
|---|---|---|---|---|---|---|---|
| $ClF_3$ Name: | | | | | | | |
| HF Name: | | | | | | | |
| $SCl_2$ Name: | | | | | | | |
| $IF_5$ Name: | | | | | | | |

## MOLECULAR GEOMETRY RESULTS

| | Lewis Structure | -- Number of -- Bonding electron Pairs | -- Number of -- Unshared electron Pairs | Hybridization | Bond Angles | Shape | Polarity |
|---|---|---|---|---|---|---|---|
| $NH_4^+$ Name: | | | | | | | |
| $PF_6^-$ Name: | | | | | | | |
| $PF_5$ Name: | | | | | | | |
| $BeCl_2$ Name: | | | | | | | |

## MOLECULAR GEOMETRY RESULTS

| | Lewis Structure | -- Number of -- Bonding electron Pairs | -- Number of -- Unshared electron Pairs | Hybridization | Bond Angles | Shape | Polarity |
|---|---|---|---|---|---|---|---|
| $SO_2$ Name: | | | | | | | |
| $SO_3$ Name: | | | | | | | |
| $CH_3Br$ Name: | | | | | | | |
| $SO_3^{2-}$ Name: | | | | | | | |

## MOLECULAR GEOMETRY RESULTS

| | Lewis Structure | -- Number of -- Bonding electron Pairs | -- Number of -- Unshared electron Pairs | Hybridization | Bond Angles | Shape | Polarity |
|---|---|---|---|---|---|---|---|
| $PO_4^{3-}$ Name: | | | | | | | |
| HCN Name: | | | | | | | |
| $AlCl_3$ Name: | | | | | | | |

## MOLECULAR GEOMETRY RESULTS

| | Lewis Structure | -- Number of -- Bonding electron Pairs | -- Number of -- Unshared electron Pairs | Hybridization | Bond Angles | Shape | Polarity |
|---|---|---|---|---|---|---|---|
| $O_3$ Name: | | | | | | | |
| CO Name: | | | | | | | |
| $H_2SO_4$ Name: | | | | | | | |
| $H_3O^+$ Name: | | | | | | | |
| $F_2C_2$ Name: | | | | | | | |

## MOLECULAR GEOMETRY RESULTS

| | Lewis Structure | -- Number of -- Bonding electron Pairs | -- Number of -- Unshared electron Pairs | Hybridization | Bond Angles | Shape | Polarity |
|---|---|---|---|---|---|---|---|
| $C_2H_2$ Name: | | | | | | | |
| $CO_2$ Name: | | | | | | | |
| $CO_3^{2-}$ Name: | | | | | | | |
| $H_2N_2$ Name: | | | | | | | |

## MOLECULAR GEOMETRY PRE-LAB WORKSHEET

This page should be completed <u>before</u> you come to class on your scheduled laboratory day.

| | Lewis Structure | -- Number of -- Bonding electron Pairs | -- Number of -- Unshared electron Pairs | Hybridization | Bond Angles | Shape | Polarity |
|---|---|---|---|---|---|---|---|
| $H_2O$ Name: | | | | | | | |
| $CH_4$ Name: | | | | | | | |
| $BF_3$ Name: | | | | | | | |
| $SF_6$ Name: | | | | | | | |
| $PCl_3$ Name: | | | | | | | |





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# SOLUTIONS LAB
# Chemistry 131

## INTRODUCTION

A solution is a homogeneous mixture of two or more substances. By homogeneous, we mean that the physical and chemical properties are uniform throughout the entire bulk of the mixture. An example can be seen by placing several crystals of table salt (NaCl) in room temperature water. We would see that the grains of salt disappear. Close examination of the water/salt drop shows that we cannot differentiate one part of the drop from another, even if we use a microscope. In contrast, examination of milk (cow's, monkey's, etc), using the eye, would lead you to believe that this can be considered a solution. This, however, is not a correct assumption. If we examine milk under a microscope, we see small bubble-like globs of fat, suspended in a clear fluid. These drops vary in size, and their composition is quite different from the clear liquid in which they are found. Milk is a mixture, but it is not homogeneous, and is therefore not a solution. It is in fact, a heterogeneous mixture.

## THEORY

### Solution Formation

A solution consists of two principal parts; the solvent and the solute. The solvent is that part of the solution which is present in the greater amount. The solute is that part which is present in the smaller amount.

We will restrict our discussion of solutions to aqueous ionic solutions. In this case water is the solvent and some ionic solid (such as NaCl) is the solute. When water and a suitable ionic solid are mixed together, the solid is seen to dissolve (disappear).

The salt crystal is composed of a series of sodium (Na) and chlorine (Cl) atoms in a repeating 3-dimensional pattern. The atoms do not exist as neutral atoms in the crystal, but rather as ions. An ion is a species which has charge, that is, positive or negative charge. It gets this charge by gaining or losing electrons. The loss of an electron yields a positively charged species, while the gain of an electron yields a negatively charged species. Therefore, table salt exists as a collection of sodium ions ($Na^+$) and chloride ions ($Cl^-$) as shown in Figure 1. The reason sodium is a positive ion (cation) and chloride is a negative ion (anion) is due to a transfer of an electron from the sodium atom to the chlorine atom. These ions are held together in the crystal by electrostatic attraction, due to their individual charges. The force of attraction is a function of the magnitudes of the charges and the distance between the ions (the farther apart, the weaker the interaction). This force of attraction which holds ions together in a crystal is given the name lattice energy.

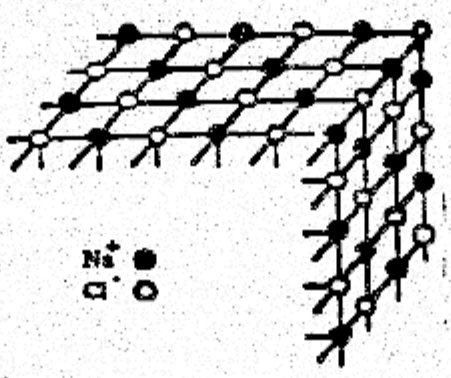



Figure 1: NaCl Structure

What is the electron configuration of the sodium ions and the chloride ions in a crystal of sodium chloride?

Are these electron configurations special (i.e., is there anything significant about them)?

When NaCl crystals are placed in water, the electrostatic attraction between the ions is broken by the water molecules. This allows the $Na^+$ and $Cl^-$ ions to move apart, and migrate into the sea of

water molecules. Since water molecules are polar (i.e., they have concentrations of "charge" on different parts of the molecule), they surround the individual sodium and chloride ions in such a way that they can still move through the solution, but do not recombine (this statement pertains to an unsaturated solution, which we shall discuss in greater depth in a future lesson.) Figure 2 shows how this might look if we could observe ions and molecules. This interaction between water molecules and ions is known as hydration. In this process, we see the "breaking" of ionic forces in the crytal, the breaking of hydrogen bonds in water and the formation of ion-dipole interactions in the solution.

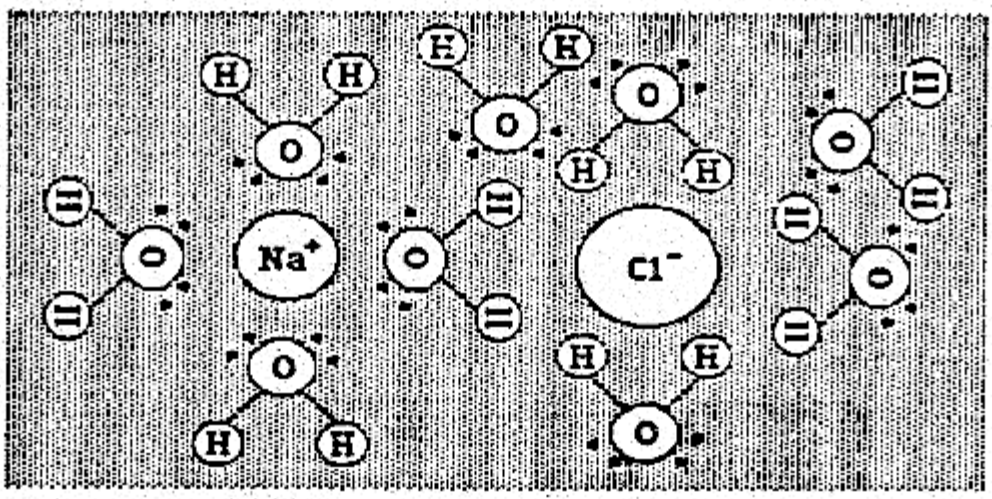



**Figure 2: Na+ and Cl- Hydration Sphere**

**Solubility of Ionic Compounds**

The driving force of the solution process is the increase in "entropy" of the system. The term "entropy" is used to describe the amount of randomness or disorder of a system. As an example, consider your dorm room as a system; does your room stay clean all the time or does it require constant effort to keep it in good shape? The fact that it does not stay clean and neat is due to the fact that the entropy of the universe wants to increase and your room is part of the universe, therefore, your room will always get messy unless you do something to prevent it.

In the solution process, we increase the disorder of the ionic solid when we put that solid in the solvent. At the same time, the attractive forces between the solute ions and the solvent molecules cause the solution to become more ordered. The amount of disorder caused by breaking up the structure of the ionic solid is greater than the amount of ordering of the solution, resulting in a net increase in entropy. Based on the above statements, all ionic solids should dissolve. However, we all know that this is not true. The reason all ionic solids do not dissolve is seen to be a function of the lattice energy of the solid and the energy required to hydrate that solid.



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In order for a solid to dissolve, the hydration energy must be larger than the lattice energy of the solid. This is the case in systems which yield exothermic mixing of solutions. In the case of endothermic solution processes, additional energy is required to overcome the lattice energy. This energy is removed from the liquid. However, there comes a point where so much additional energy is needed to overcome the lattice interactions, that the liquid cannot provide enough energy and the solid will not dissolve.

You will investigate the energy liberated or absorbed during the solution process with the aid of a "diode" attached to a multimeter. Endothermic mixing causes the meter reading to increase, while exothermic reactions cause the meter reading to decrease.

**Factors Which Influence Lattice and Hydration Energies**

The smaller an ion, the more concentrated the electrical charge compared to a large ion. Thus, we would expect small ions to attract water molecules more intensely than large ions. By the same token, we would also expect the small ion to interact more intensely with other ions in a solid as well. Thus, a small ion will increase both the hydration and lattice energies.

Ions with larger charges will exert a greater force of attraction on other ions than ones with small charges. Therefore, increasing atomic charge will also increase hydration and lattice energies.

**Conductivity**

Ions can move in solution implying that charge (determined by the presence or lack of electrons) can be carried through the bulk of a solution. If an electromotive force, in the form of two leads from a battery, is brought into contact with an ionic solution, we observe the movement of ions toward the leads of the battery. We also observe a current in the external circuit. In this experiment, the external circuit current will be used to illuminate a light emitting diode (LED).

**LAB PROCEDURE**

**A. Conductivity of Solutions**

(1) Construct your conductivity tester as shown in Figure 3. Prop the LED up, by placing it in a plastic straw, and inserting the free end of the straw in the plastic tray provided.

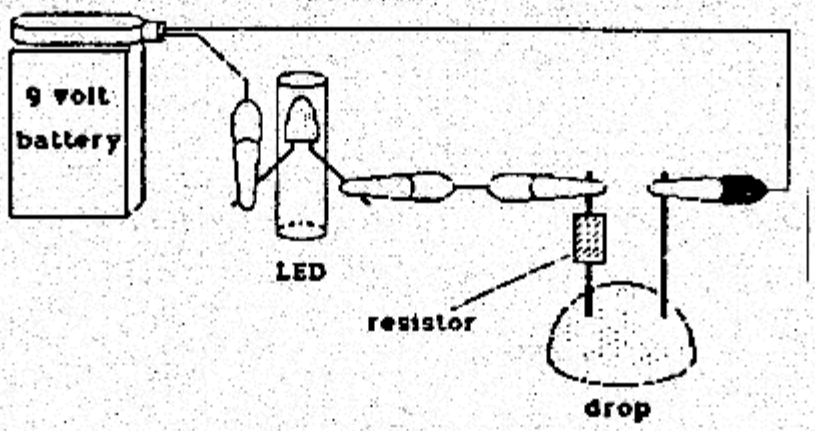



Figure 3: Conductivity Tester.

(2) Place the electrodes in contact with a small amount of crystalized NaCl, KCl and $AlCl_3$.

Does the LED light up? _____

(3) Make a large drop of deionized water on your acetate sheet (the large drop should consist of about 4 small drops).

(4) Insert the ends of your conductivity tester into the deionized water.

Does the LED light up? _____

(5) Now, make a 2 x 5 matrix of large drops, as shown in Figure 4.

top row o o o o o

bottom row o o o o o

each circle consists of 4 small drops

Figure 4: Drop arrangement.

(6) To the top row, sequentially add one crystal (about the size of a period on this page) of NaCl, KCl, AgCl, $CaCl_2$ and $AlCl_3$.

(7) To the bottom row, add several crystals of each chemical.

(8) The first drop in the top and bottom rows contains NaCl in solution. Insert the battery leads into the top drop and take note of the brightness of the LED.

How bright does it seem?

(9) Wipe off the leads with a paper towel, and place them into the bottom drop of NaCl solution.

Compare the brightness of the LED in each NaCl case; is there a difference? If so, why do you think there is a difference?

(10) Perform steps (8) and (9) for each of the other sets of drops. Write your results below.

| | KCl | AgCl | $CaCl_2$ | $AlCl_3$ |
|---|---|---|---|---|
| Top Drop | | | | |
| Bottom Drop | | | | |
| Comparison | | | | |

**NOTE**: Make sure you wipe off the ends of your leads before you put them in a new solution.

## B. Endothermic and Exothermic Mixing

(1) Set up the meter/diode test apparatus as shown in Figure 5. A diode is an electronic device that allows current to flow in only one direction. You will use a special type of diode called a thermistor. A thermistor is a semiconductor material which has resistance proportional to $^1/_T$. Thus you observe increased resistance with decreased temperature.

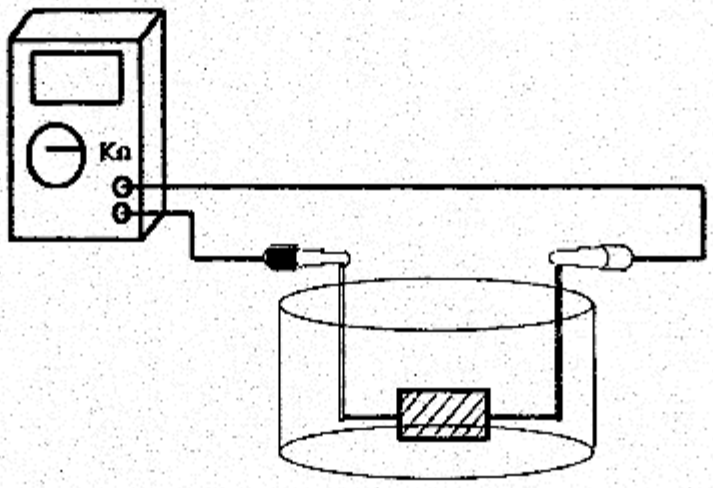



**Figure 5: Equipment Arrangement**

(2) Prior to connecting the meter leads to the diode, turn the meter to the "kilo-ohms" setting and press the button in the center of the dial until "kilo-ohms" is displayed with only one space to the right of the decimal point. After you have set the meter, connect the diode to the meter leads. You should obtain a reading on the meter. If you obtain an overload reading on the meter simply reconnect the meter leads to the opposite leads of the diode.

(3) Fill one of the wells of the 24-well tray half-full of deionized water. Place the diode into the water and allow the meter reading to stop fluctuating.

(4) Add a small amount of $NH_4Cl$ to the well and observe the change in the meter reading. Remember that endothermic mixing causes the meter reading to increase, while exothermic reactions cause the meter reading to decrease.

(5) Remove the diode from the solution, and thoroughly rinse it with deionized water.

(6) Perform the same procedure for NaCl, KCl, $MgCl_2$, $CaCl_2$, and $AlCl_3$ and record your results in chart form on the following page. Classify each system as either endothermic or exothermic.

**HEAT OF SOLUTION DATA**

A. $NH_4Cl$

B. NaCl

C. KCl

D. $MgCl_2$

E. $CaCl_2$

F. $AlCl_3$

**CONCLUSION**

1. All the solids you used are ionic. Identify the ions and give electron configurations for each ion in the five solids.

2a. Did all the solids dissolve?

2b. If any did not, what might explain the fact that it did not dissolve?

3. What would you expect to take place if KBr, NaCl and $MgCl_2$ were mixed together in a beaker of water?

4. How does $CaCl_2$ exist in solution? (Hint: Figure 2).

5. What periodic properties/concepts explain the formation of an ionic compound?

6. Which salts produced endothermic mixing and which produced exothermic mixing? **In terms of lattice energy and hydration energy explain** why we see energy being released or absorbed in the mixing of these salts with water.

**Prelaboratory Exercise**

1. What's the differences between a solution and mixture?

2. What is the driving force in the dissolution process?

3. What is the purpose of the light emitting diode in this experiment?

4. What is the thermistor used for in part "B"?

5. What's the difference between an endothermic mixing process and an exothermic mixing process?

# ACID RAIN
# Chemistry
# 131

## INTRODUCTION

The increased acidity of lakes and natural waterways in recent years due to acid rain is a major concern in the United States, Canada and several European nations. Acid rain is generated when gases such as sulfur dioxide ($SO_2$) and nitrogen dioxide ($NO_2$) are hydrolyzed in water. The high acid content of clouds and waterways has damaged forests and the ability of lakes to sustain aquatic life.

In this experiment, you will investigate the effects of these pollutant gases and naturally occurring carbon dioxide ($CO_2$) on the acid content of water. This will be done qualitatively using Yamada indicator in water as a probe for changes in hydrogen ion concentration. You will also quantitatively determine the effects of each gas by titrating water acidified by the gases to determine the acid content produced.

## THEORY

### Definitions

Acid: For this lab, we will define an acid as any substance that dissociates in water to give hydrogen ions, $H^+$.

Acid Content: Acid content is a measure of the stoichiometric number of hydrogen ions available from an acid. Nitric acid, $HNO_3$, can provide only one hydrogen ion per molecule of acid, while sulfuric acid, $H_2SO_4$, produces two hydrogen ions per molecule of acid.

Acid content may be measured in several ways. Indicators are chemicals which respond to the hydrogen ions in solution by changing color, providing visual assessment of hydrogen ion concentration. A much more accurate measurement can be made by "titrating" the solution. This is done by measuring the amount of a base (of known concentration) required to completely react with the acid. You will use both methods in this lab.

**Generation of Gases**

Carbon dioxide, sulfur dioxide, and nitrogen monoxide, may be formed by reacting certain aqueous salts with an acid. Generation of each gas occurs via a complex chemical mechanism. The purpose of this experiment is not to investigate these mechanisms but to investigate the effect each of these gases has on water.

Carbon dioxide, $CO_2$, will be generated by reacting a solution of sodium carbonate, $Na_2CO_3$, with nitric acid, $HNO_3$. In solution, sodium carbonate exists as sodium ions and carbonate ions:

$$Na_2CO_{3(s)} \longrightarrow 2Na^+_{(aq)} + CO_3{}^{2-}_{(aq)} \qquad (1)$$

In an acidic solution, the carbonate ion will combine with hydrogen ions to form the more stable carbonic acid:

$$CO_3{}^{2-}_{(aq)} + 2H^+_{(aq)} \rightleftharpoons H_2CO_{3(aq)} \qquad (2)$$

When a solution of carbonic acid is made more acidic, it decomposes to form carbon dioxide and water:

$$H_2CO_{3(aq)} \rightleftharpoons CO_{2(g)} + H_2O_{(l)} \qquad (3)$$

To increase the acidity of the $Na_2CO_3$ solution, a strong acid ($HNO_3$) is added, and the gas, $CO_2$, is released. Sulfur dioxide and nitrogen monoxide will be produced in a similar fashion. In the natural environment, these gases are generated by a variety of sources. However, the gases are identical to those generated in this experiment.

**Concentration of Gases**

The balanced equations for the generation of $CO_{2(g)}$ from sodium carbonate and $SO_{2(g)}$ from sodium sulfite show that different numbers of moles of gas are produced than the number of moles of $NO_{(g)}$ produced from sodium nitrite. For every mole of $Na_2CO_3$, one mole of $CO_2$ is produced. For every mole of $Na_2SO_3$, one mole of $SO_2$ is produced. However, for every 3 moles of $NaNO_2$, only 2 moles of NO is produced.

To compare the acid content produced in water from each of these gases, you need to insure that equal moles of gas are produced in your experiment. You will do this by diluting the aqueous solutions of the salts based on the balanced chemical equations.

**Effect of Gases on Water**

The gases that you generate will react with water in a drop of Yamada indicator to produce acids as follows:

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \qquad (4)$$

(Note: This is the reverse of equation 3.)

Yamada indicator will be violet to blue colored if the solution is basic, green for neutral solutions, and yellow to red for acidic solutions.

Sulfur dioxide reacts in a similar fashion to form sulfurous acid:

$$SO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2SO_{3(aq)} \qquad (5)$$

We'll not consider the effect of nitrogen monoxide on water because it quickly reacts with oxygen in the air to form nitrogen dioxide. Nitrogen dioxide then reacts with water forming nitric acid and nitrous acid:

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

$$2NO_{2(g)} + H_2O_{(l)} \rightleftharpoons HNO_{3(aq)} + HNO_{2(aq)} \qquad (6)$$

**Generation of Sulfuric Acid**

A current area of scientific study is how sulfuric acid is formed in the atmosphere. Two hypotheses have been identified. The first states that sulfuric acid forms within water droplets when sulfurous acid is oxidized by nitrous acid:

$$2H_2SO_{3(aq)} + 2HNO_{2(aq)} \text{ -----> } 2H_2SO_{4(aq)} + N_2O_{(aq)} + H_2O_{(l)} \qquad (7)$$

The second hypothesis is that sulfurous acid is simply oxidized to sulfuric acid by atmospheric oxygen. The difference in these two hypotheses is the presence of nitrous acid. You will design an experiment to test each hypothesis, and draw your own conclusions.

**EXPERIMENTAL**

**A. CONCENTRATION OF GASES GENERATED**

1. Compare the balanced equations for generating $CO_2$, $SO_2$, and NO from their respective aqueous salts. The balanced equation for $CO_2$ has been provided (equations 1-3). You must write and balance equations for $SO_2$ and NO (*see paragraphs C.1.a and D.1.a below*). Based on these equations, determine the ratio of moles of aqueous salt to moles of gas produced from each salt. You must adjust the concentrations of the salt solutions to insure the same number of moles of gas will be produced in all three cases. Write the ratios below:

$Na_2CO_{3(aq)}/CO_{2(g)}$ $Na_2SO_{3(aq)}/SO_{2(g)}$ $NaNO_{2(aq)}/NO_{(g)}$

2. Your ratios should indicate that sodium sulfite and sodium carbonate produce the same amount of gas, while sodium nitrite produces comparatively less. Both the sodium carbonate and sodium sulfite must be diluted to produce the same amount of gas as sodium nitrite. Based on the ratios from paragraph A.1., calculate the new concentration (in molarity) of sodium carbonate and sodium sulfite solutions needed (the stock solutions are all 1.0 M):

New $Na_2CO_3$ Concentration

New $Na_2SO_3$ Concentration

a. Now use the relationship, $M_1V_1 = M_2V_2$, to calculate the number of drops of aqueous salt solution and deionized water that must be mixed to obtain the required concentrations. Recall that M is molarity of the solution, set $V_1$=1 drop and solve for $V_2$. $V_2$ is the new total volume (in drops) required to obtain the appropriate concentration. By using $V_2$-1 drop, you will obtain the number of drops of water to add to dilute the solution (the -1 accounts for your initial drop of solution). For both $Na_2CO_3$ and $Na_2SO_3$, show $V_2$, the number of drops of 1.0 M stock solution, and the number of drops of deionized water mixed to obtain the correct concentration:

Dilution Data $Na_2CO_3$

Dilution Data $Na_2SO_3$

**B. EFFECT OF $CO_2$ ON WATER**

1. Dilute your stock solution of sodium carbonate as determined by the above calculations to obtain the necessary concentration. Do this by placing several drops of your 1.0 M stock solution on a clean area of the reaction surface and add the correct number of drops of deionized water.

2. Place two drops of Yamada indicator in the petri dish.

3. Rinse an unlabeled microburet several times with deionized water and then use it to transfer your diluted $Na_2CO_3$. Place two drops of the diluted $Na_2CO_3$ near but not touching the drop of indicator and cover the dish. It will be important to have the same drop size in each section so the <u>same</u> unlabeled microburet must be used each time.

4. Carefully lift an edge of the lid and add one drop of 3 M $HNO_3$ directly on top of the drop of $Na_2CO_3$. Describe what happens to both drops. Continue to make observations for at least two minutes.

a. Evolution of carbon dioxide will be indicated by the appearance of bubbles (equations 1-3). The color change of the indicator is due to the formation of carbonic acid as the carbon dioxide dissolves into the drop and reacts with the water.

b. Carbonic acid is a weak acid. This means that it doesn't dissociate completely to give 100% hydronium ($H_3O^+$) ions and bicarbonate ($HCO_3^-$) ions. Instead, it partially dissociates, and an equilibrium is established:

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-{}_{(aq)} \quad (8)$$

5. Repeat steps 2-4 using 15-20 drops of freshly drawn deionized water instead of the indicator. Rinse out an unlabeled microburet with deionized water. After two minutes, insert your cleaned, unlabeled microburet through the entry port to remove some of the acidified water. Place three drops of this solution on the reaction surface and add one drop of indicator to it.

6. Titrate this solution of aqueous carbonic acid to determine how much acid was produced by the carbon dioxide gas. The procedure to titrate is:

a. First empty an unlabeled microburet and rinse it several times with deionized water.

b. Place 10-15 drops of freshly drawn 0.001 M sodium hydroxide (NaOH) onto the reaction surface and siphon it up with the clean, unlabeled microburet. Always transfer the acidified water and NaOH with the **same** microburet to ensure the drop sizes are always the same. We will assume that **one drop has a volume of $2.0 \times 10^{-5}$ L.**

c. Carefully add the base (NaOH) one drop at a time to the acidified water on your reaction surface. Continue to carefully add dropwise until the indicator turns green (indicating the solution is no longer acidic). Count the number of drops added. At this "equivalence point", the number of moles of base added equals the number of moles of hydrogen ions present in solution.

d. If the indicator turned blue, you have passed the equivalence point. Assume that $^1/_2$ of a drop of base would have yielded the green color, then, total the number of drops of base added.

e. Record the colors of your acidified water with indicator before and after the titration. Also record the number of drops NaOH added.

Color of acidified water from generation of $CO_2$

**Before** **After**

Number of drops 0.001 M NaOH added:

7. Clean and dry the petri dish.

## C. EFFECT OF $SO_2$ ON WATER

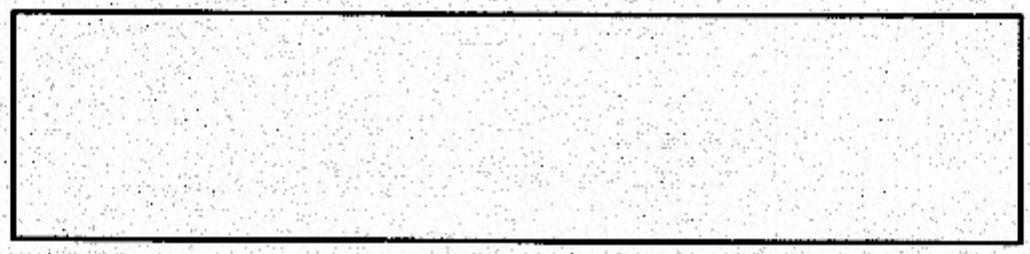
1. Use sodium sulfite ($Na_2SO_3$) to perform an experiment showing the effect of $SO_2$ on water. Follow the same procedure as you used in showing the effect of $CO_2$ on water (section B). *(Remember to change the concentration of your stock solution to allow for generation of equal moles of $SO_2$, $CO_2$, and NO.)*

**CAUTION: ALWAYS NEUTRALIZE THE POISONOUS $SO_2$ BY ADDING 3.0 M AMMONIUM HYDROXIDE ($NH_4OH$) TO THE PETRI DISH PRIOR TO REMOVING THE LID AND AFTER YOU HAVE REMOVED YOUR ACIDIFIED SAMPLE.**

a. The reaction of $Na_2SO_3$ and acid is similar to the reaction of acid and $Na_2CO_3$ (equations 1-3). Write the chemical equations for the generation of $SO_{2(g)}$ from $Na_2SO_{3(aq)}$:

b. What acid is formed when $SO_2$ dissolves in water?

c. The formation of this acid is analogous to the formation of carbonic acid. Write the chemical reaction that describes the formation of acid when water reacts with $SO_2$.



d. After diluting your stock solution of sodium sulfite, transfer two drops of the diluted solution with an unlabeled microburet (don't forget to rinse it first with deionized water) to the petri dish. Add nitric acid to generate $SO_2$ and show its effect on a drop of Yamada indicator. **REMEMBER TO NEUTRALIZE THE $SO_2$ BEFORE LIFTING THE LID OFF!**

e. Compare the effect of $CO_2$ versus $SO_2$ on the indicator.

2. Repeat the generation of $SO_2$ using freshly drawn deionized water and your diluted $Na_2SO_3$. Use the same amount of deionized water as you used in B.5.b. Collect a sample after two minutes and titrate this sample using 0.001 M NaOH. The titration procedure is outlined in paragraphs B.6.a - B.6.e. **REMEMBER TO NEUTRALIZE THE $SO_2$! Record your results below:**

Color change:

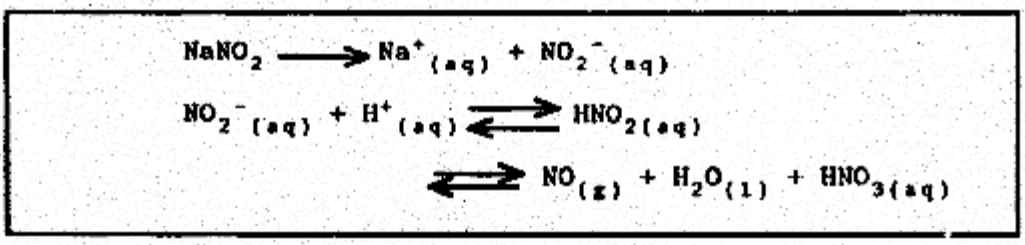
Number of drops base added:

3. Clean and dry the petri dish.

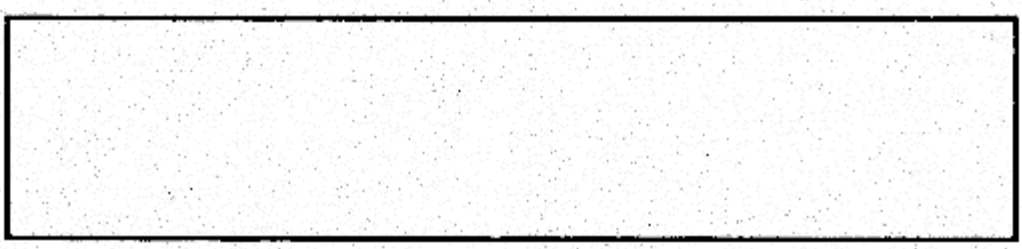
**D. EFFECT OF $NO_2$ ON WATER**

1. Perform an experiment to show the effect of nitrogen dioxide ($NO_2$) on water using 1.0 M $NaNO_2$. **YOU MUST NEUTRALIZE THE $NO/NO_2$ REMAINING IN THE PETRI DISH WITH $NH_4OH$!**

a. The following two equations have been filled in for you. Fill in the last equation for the formation of NO in an acidified drop of water:




b. Write the equation for the reaction of $NO_2$ and water.



c. Generate NO to show its effect on water. Describe what you see:

d. The brown colored gas produced is $NO_2$. Nitrogen monoxide (NO) is an unstable gas, and is immediately oxidized to $NO_2$ by atmospheric oxygen in the petri dish. Nitrogen dioxide is a poisonous gas. IT TOO MUST BE NEUTRALIZED BY ADDING $NH_4OH$ TO THE PETRI DISH, followed by a wait of approximately thirty seconds.

2. After neutralizing any excess $NO_2$, clean and dry the petri dish.

3. Titrate a sample of water acidified with $NO_2$. Record your results below. REMEMBER TO NEUTRALIZE THE POISONOUS $NO_2$ GAS USING $NH_4OH$ AFTER REMOVING YOUR ACIDIFIED WATER SAMPLE, BUT PRIOR TO REMOVING THE PETRI DISH LID!

4. Clean and dry the petri dish.

**E. FORMATION OF SULFURIC ACID**

Design an experiment to test the two hypotheses about the formation of sulfuric acid in a rain drop. The experiment should have at least three parts:

a. Procedure (experimental). Outline your procedure to illustrate what you will do. Drawings may be helpful.

b. Observations (results). Collect your observations in a way that is easily related to your procedure.

c. Conclusions. Evaluate each hypothesis in light of the observations made during your experiment.

To help you get started, you have been provided with 0.1 M $Ba(NO_3)_2$. This will be used as a probe to detect the presence of $SO_4^{2-}$ by giving a white precipitate, indicating the formation of sulfuric acid as opposed to sulfurous acid.

After completing your experiment and recording all necessary information, clean and dry the petri dish and reaction surface. Rinse out the unlabeled microburet several times with deionized water, and perform any other necessary lab clean up.

**RESULTS**

1. Calculate the number of moles of acid produced from the generation of each gas. Use the data from each titration that you performed, and recall that at the equivalence point, the number of moles of acid present equals the number of moles base added.

a. From $CO_2$:

b. From $SO_2$:

c. From $NO_2$:

2. Make a table listing each gas, the acid content produced, and the indicator colors at the beginning and end of each titration. What comparisons can be made concerning the capability of each gas to affect the environment?

**CONCLUSIONS**

1. What can be concluded about the capability of each gas to increase the acid content of water?

2. Write balanced equations to explain how each gas forms an acid with water.

3. What can be concluded about the acidity of all rain water given that carbon dioxide is a naturally occurring gas?

4. Explain why acid rain is primarily a problem in the Eastern United States and Canada as opposed to the Western United States.

5. How do you think we can solve the acid rain problem for the long term?

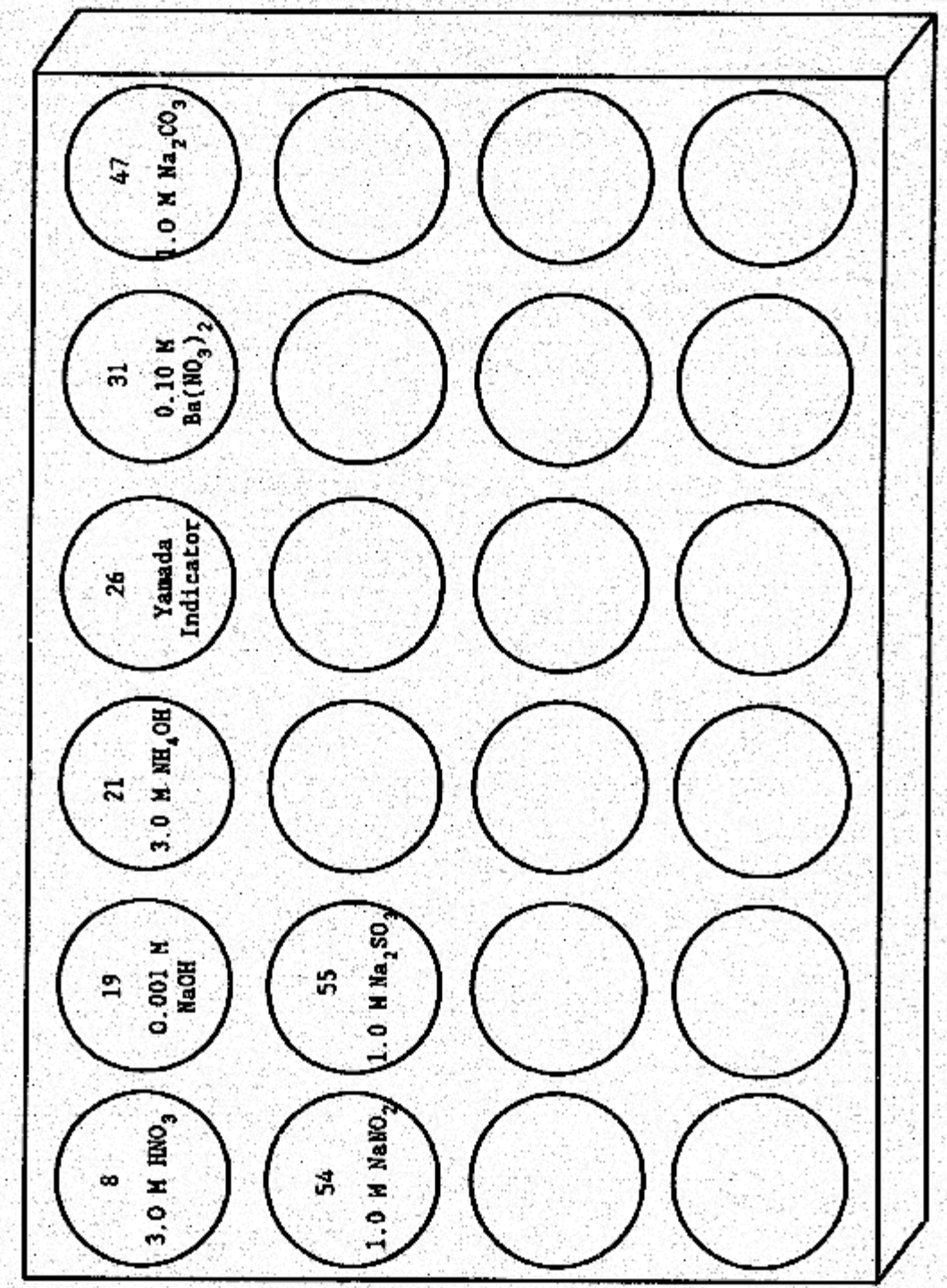
## PRE LAB EXERCISE

1. List those gases that react with atmospheric water to cause it to be acidic.

2. Write the equation for the formation of acid when $SO_2$ reacts with water (hydrolyzes):

3. What is "acid content"?

4. Do HCl and $H_2SO_4$ have the same acid content?


47
1.0 M $Na_2CO_3$
31
0.10 M $Ba(NO_3)_2$
26
Yamada Indicator
21
3.0 M $NH_4OH$
19
0.001 M NaOH
55
1.0 M $Na_2SO_3$
8
3.0 M $HNO_3$
54
1.0 M $NaNO_2$

110

# SPECTROMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT
## Chemistry 131

**INTRODUCTION**

Do all chemical reactions go to completion? Do they progress until all of one reactant is completely used up or do they proceed to only a limited extent, or for that matter not at all? These are important questions concerning chemical equilibria which will be discussed in this laboratory.

A condition of equilibrium exists in a chemical system when two opposing reactions occur simultaneously at the same rate. As a result, products are being formed from reactants as quickly as reactants are being produced from products. It is important to note that after equilibrium has been established, there will be some products formed and some reactants remaining.

Not all reactions go to completion. An example of one that does go to completion is the dissociation of a strong acid, such as HCl, in water:

$$HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \qquad (1)$$

The single arrow indicates practically complete product formation ($H_3O^+$ and $Cl^-$); we would expect no significant amount of reactants to remain if one mole of HCl is reacted with one mole of water.

On the other hand, a system at equilibrium such as the reaction of iron(III) ion with the thiocyanate ion:

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)} \qquad (2)$$

is expressed using two arrows pointing in opposite directions to indicate a state of equilibrium.

Equation (2) is a net ionic equation where $Fe^{3+}$ and $SCN^-$ represent the reactants and $FeSCN^{2+}$ represents the product. You cannot simply go to the corner store and pick up some $Fe^{3+}$ or $SCN^-$ ions. In this lab the $Fe^{3+}$ ion comes from an $Fe(NO_3)_3$ (iron (III) nitrate) solution and the $SCN^-$ ion comes from a KSCN (potassium thiocyanate) solution. When these species are mixed in an aqueous solution, the following ions form:

$$Fe^{3+}_{(aq)},\ NO_3^-{}_{(aq)},\ K^+_{(aq)},\ \text{and}\ SCN^-_{(aq)}$$

The $K^+(aq)$ and $NO_3^-(aq)$ ions remain in solution unchanged from reactants to products. Ions that remain unchanged in the overall reaction are known as spectator ions and are not shown in the net ionic equation.

You can derive the correct equilibrium constant expression, $K_c$, for equation (2):

$$K_c = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} \qquad (3)$$

$K_c$ is the ratio of equilibrium *product* concentrations (the brackets denote concentrations in molarity) to equilibrium *reactant* concentrations. Each concentration term is raised to a power given by the number of moles of that substance appearing in the balanced chemical equation. In equation (3), all molar coefficients are equal to 1.

**OBJECTIVES**

There are three things you should accomplish during this laboratory:

1. Learn how a standard laboratory instrument, in this case a spectrometer, is used to collect data on chemical reactions.

2. Determine the equilibrium constant for a chemical reaction.

3. Determine $\Delta H$, $\Delta S$, and $\Delta G$ for a chemical reaction.

**BACKGROUND**

In this experiment you will determine the value of the equilibrium constant ($K_c$) for the reaction:

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$$

Unfortunately for us, we do not know the equilibrium concentrations of $Fe^{3+}$, $SCN^-$, or $FeSCN^{2+}$, but only the initial concentrations of the two reactants, $Fe^{3+}$ and $SCN^-$. The equilibrium concentrations of $FeSCN^{2+}$ is determined colorimetrically using the spectrometer. Iron(III) thiocyanate ion is a red-orange color and the intensity of color increases with increasing $FeSCN^{2+}$ concentration in solution. To determine the equilibrium concentrations of $Fe^{3+}$ and $SCN^-$, we use the fact that $Fe^{3+}$ and $SCN^-$ can exist either as uncomplexed (free) ions or as complexed $FeSCN^{2+}$. The equilibrium concentrations of $Fe^{3+}$ and $SCN^-$ are found by the difference between the initial concentration of ion added to the solution and the concentration of complexed ion ($FeSCN^{2+}$).

This reaction must be conducted in a moderately strong acid solution to prevent the formation of the $FeOH^{2+}$ ion:

$$Fe^{3+}_{(aq)} + H_2O_{(l)} \rightleftharpoons FeOH^{2+}_{(aq)} + H^+_{(aq)}$$

The $FeOH^{2+}$ ion absorbs light at the same wavelength as $FeSCN^{2+}$. To have $FeOH^{2+}$ present would cause considerable experimental error. According to Le Chatelier's principle, addition of $H^+$ shifts this equilibrium to the left, minimizing the formation of $FeOH^{2+}$.

You will use a Spectronic 20 spectrometer to measure the amount of light absorbed (absorbance) by the $FeSCN^{2+}$ solution. The absorbance, **A**, of the solution is proportional to the $FeSCN^{2+}$ concentration ($[FeSCN^{2+}]$) according to the following equation:

$$A = \epsilon \ell [FeSCN^{2+}] \qquad (4)$$

where $\epsilon$ and $\ell$ are empirically determined constants. This relationship is known as **Beer's Law**; $\epsilon$ is the molar absorptivity, an intensive property of the light absorbing species, and $\ell$ is the effective path length, or distance the light must travel through the solution in the spectrometer. For aqueous solutions of $FeSCN^{2+}$, the molar absorptivity is $\epsilon = 4.70 \times 10^3\ M^{-1}cm^{-1}$ at the wavelength of maximum absorbance (447 nm). The path length is the internal diameter of the special tube (cuvette) used to hold the solution. You will use a cuvette with $\ell = 1.17$ cm. Thus, for aqueous solutions of $FeSCN^{2+}$ the concentration of $FeSCN^{2+}$ is given by:

$$[FeSCN^{2+}] = \frac{A}{\epsilon \ell} = \frac{A}{5.50 \times 10^3\ M} \qquad (5)$$

Although absorbance can be read directly, the scale is nonlinear. This makes it difficult to read, and very easy to record incorrect data. Instead, use the percent transmittance, (%T), scale since it is linear and easier to read.

You may then determine the absorbance:

$$A = -\log T \qquad (6)$$

(Note: Use T in equation 6 and not % T.) A sample of very high color intensity absorbs virtually all the light from the spectrometer. This gives 0% transmittance or infinite absorbance. Conversely, as the sample solution becomes more dilute, more light is transmitted through the solution. At zero concentration the transmittance of light is 100% (T=1) and the absorbance is zero.

You now know how to calculate the absorbance (equation 6) and thus, you use this number to determine the equilibrium concentration of $FeSCN^{2+}$ (equation 5). From equation (2), we know that the equilibrium concentration of $Fe^{3+}$ ($[Fe^{3+}]_{eq}$) may be found by:

$$[Fe^{3+}]_{eq} = [Fe^{3+}]_{initial} - [FeSCN^{2+}]_{eq} \qquad (7)$$

**TEMPERATURE EFFECTS**

The dependence of the equilibrium constant on temperature indicates whether the reaction is endothermic or exothermic. If the equilibrium constant decreases as the temperature is increased, we know that formation of the products compared to the reactants is less favored at this temperature than at the lower temperature; thus, according to Le Chatelier's principle, the reaction is exothermic. By a similar process of deduction, we could conclude that if the equilibrium constant increases as the temperature increases, the reaction must be endothermic.

Recall from your study of thermochemistry that:

$$\Delta G = \Delta H - T\Delta S \qquad (8)$$

and

$$\Delta G = -RT \ln K_c \qquad (9)$$

From data you collect in this experiment, you can solve for all these thermochemical parameters:

1. By measuring transmittance and calculating equilibrium concentrations, you can find the value for $K_c$ and from this you can solve for $\Delta G$ using equation 9.

2. By studying the reaction at different temperatures and calculating the equilibrium constant, it is possible to calculate the heat of reaction, $\Delta H$, and the change in entropy $\Delta S$.

By substituting the value of $\Delta G$ from equation 9 into equation 8 you obtain:

$$-RT \ln K_c = \Delta H - T\Delta S \qquad (10)$$

Dividing both sides by -RT you obtain:

$$\ln K_c = -\left[\frac{\Delta H}{R}\right] x \left[\frac{1}{T}\right] + \frac{\Delta S}{R} \qquad (11)$$

This equation is in the form of y = mx + b in which

$$y = \ln K_c;\ x = 1/T;\ b = \frac{\Delta S}{R} \text{ and } m = -\frac{\Delta H}{R}.$$

The reciprocal of the temperature (1/T) in Kelvin plotted versus the natural logarithm of the equilibrium constant ($\ln K_c$), should be a straight line with a slope of $-\Delta H/R$ where R is the gas constant, 8.314 J/(mole K) and $\Delta H$ is the heat of reaction. What does the slope of this line tell you about the exothermicity or endothermicity of the reaction?

3. Once $\Delta G$ and $\Delta H$ are calculated, it's a simple matter to find $\Delta S$ from Equation (8). You may also determine $\Delta S$ from the y-intercept of the graph mentioned in paragraph 2 (y-intercept equals $\Delta S/R$).

## EXPERIMENTAL

NOTE: $Fe(NO_3)_3$ IS ACIDIC. BOTH $Fe(NO_3)_3$ and KSCN WILL STAIN THE LAB BENCHES. BE CAREFUL WITH THESE SOLUTIONS AND WIPE UP YOUR SPILLS IMMEDIATELY. SPONGES, CLEANSER AND ELBOW GREASE ARE THE ONLY METHOD YOU WILL USE TO CLEAN THE LAB BENCHES.

### A. PART 1: TRANSMITTANCE MEASUREMENT

1. Thoroughly clean, rinse and dry eight 250 mL or 100 mL beakers. Number the beakers one through eight with a grease pencil. Remember, all of your solutions will have the same volume of 40.00 mL.

2. Using a clean beaker, obtain about 100 mL of 0.00200 M KSCN stock solution from the side shelf. In another beaker obtain about 100 mL of a mixed solution which is 0.00300 M with respect to $Fe(NO_3)_3$ and 2.00 M with respect to $HNO_3$. Record the exact concentration of the stock solutions used.

3. Fill your clean and marked beakers with these reagents in accordance with Table 1. Use a graduated cylinder to measure the reagents and de-ionized water.

TABLE 1

| BEAKER | $Fe(NO_3)_3/HNO_3$ | KSCN | De-ionized $H_2O$ | Total VOLUME |
|---|---|---|---|---|
| 1 | 10.00 mL | 4.00 mL | 26.00 mL | 40.00 mL |
| 2 | 10.00 mL | 6.00 mL | 24.00 mL | 40.00 mL |
| 3 | 10.00 mL | 8.00 mL | 22.00 mL | 40.00 mL |
| 4 | 10.00 mL | 10.00 mL | 20.00 mL | 40.00 mL |
| 5 | 10.00 mL | 12.00 mL | 18.00 mL | 40.00 mL |
| 6 | 10.00 mL | 14.00 mL | 16.00 mL | 40.00 mL |
| 7 | 10.00 mL | 16.00 mL | 14.00 mL | 40.00 mL |
| 8 | 10.00 mL | 18.00 mL | 12.00 mL | 40.00 mL |

4. Mix each solution with a clean, dry stirring rod; rinse and dry your stirring rod after each solution. Record the actual volumes used.

5. Be sure that the wavelength is set to 447 nm on the SPEC 20. Calibrate the Spec 20 using the instructions on the last page of this handout. Now you are ready to measure the percent transmittance of the solutions.

6. Measure the temperature of one of the solutions. Assume that the temperature is the same for all beakers. Record the temperature below.

7. Obtain a cuvette from your instructor.

8. Be sure the cuvette is clean. Fill the cuvette up to the bottom of the frosted circle with solution from beaker 1.

9. Place the cuvette in the SPEC 20 with the frosted circle aligned with the mark on the SPEC 20. Close the cover over the cuvette.

10. Record the percent transmittance. Use TABLE 2 to record the percent transmittance.

**NOTE:** Don't allow the cuvette to remain in the SPEC 20 for an extended period for it will warm the solution and change the reading.

11. Remove the cuvette form the SPEC 20. Discard the solution down the sink.

12. Rinse the cuvette with a small (less than 1 mL) amount of solution from the next beaker. Discard the rinse solution. Fill the cuvette with fresh solution from the same beaker and measure the percent transmittance as in steps 9 through 11.

**NOTE:** Be sure to rinse out the cuvette with the solution you are going to measure next. This will avoid contamination of the new solution to be measured by the previous solution. Also, don't rinse the cuvette with water between measurements; lingering water will dilute the solution to be measured resulting in an incorrect reading.

13. Repeat the procedure in step 12 for the remaining beakers numbered 3 through 8.

**B. PART 2: TEMPERATURE DEPENDENCE OF $K_c$**

1. Set up a cold and a hot water bath.

2. Fill the blue pneumatic trough with an ice water solution. (Add approximately one 400 mL beaker of ice.)

3. Fill another pneumatic trough with hot tap water.

4. Place beakers 1 through 4 in the cold bath for at least ten minutes.

5. Place beakers 5 through 8 in the hot water bath for at least ten minutes.

**NOTE:** The next steps must be carried out in a **TIMELY FASHION** to prevent large temperature changes from occurring.

6. Remove beaker 5 from the hot water bath. At this time measure the temperature of the solution. Record this temperature below.

7. Fill the cuvette and measure the percent transmittance as you did in Part 1. Record the percent transmittance.

8. Repeat steps 6 and 7 with beakers 6 through 8. Be sure to rinse the cuvette with the solution before measuring the percent transmittance of the solution.

9. Now you can measure the percent transmittance of beakers 1 through 4, in the cold water bath, following the procedure in this part steps 6 through 8.

TABLE 2

ROOM TEMPERATURE: TEMPERATURE= °C

| BEAKER | %T | A | INITIAL $[Fe^{3+}]$ | INITIAL $[SCN^-]$ | EQUILIBRIUM $[Fe^{3+}]$ | EQUILIBRIUM $[SCN^-]$ | EQUILIBRIUM $[FeSCN^{2+}]$ | $K_c$ |
|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | |
| 2 | | | | | | | | |
| 3 | | | | | | | | |
| 4 | | | | | | | | |
| 5 | | | | | | | | |
| 6 | | | | | | | | |
| 7 | | | | | | | | |
| 8 | | | | | | | | |

COLD TEMPERATURE: TEMPERATURE= °C

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | |
| 2 | | | | | | | | |
| 3 | | | | | | | | |
| 4 | | | | | | | | |

HOT TEMPERATURE: TEMPERATURE= °C

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 5 | | | | | | | | |
| 6 | | | | | | | | |
| 7 | | | | | | | | |
| 8 | | | | | | | | |

**LABORATORY REPORT REQUIREMENTS**

The lab report must include the following:

1. Statement of objective

2. Theory (1-2 pages)

3. Results - Since there are many calculations that must be made on this lab, the use of a spreadsheet program is recommended. Using the data collected from Part 1 and Part 2 calculate the following and include it in Table 2.

a. Absorbance from the transmittance data (show a sample calculation below):

b. Initial concentrations of $Fe^{3+}$, and $SCN^-$ (show a sample calculation below):

c. Equilibrium concentrations of $Fe^{3+}$, $SCN^-$, and $FeSCN^{2+}$ (show a sample calculation):

d. Equilibrium constant at all three temperatures for equation (2) (show a sample calculation):

e. The average $K_c$ at each temperature.
$K_c$ at room temperature:
$K_c$ at cold temperature:
$K_c$ at hot temperature:

f. $\Delta G$ using equation (9):

g. $\Delta H$ using a graph of 1/T versus ln $K_c$ and using equation 11.

h. $\Delta S$ from the y-intercept of the same graph and from equation (11):

Place this data into Table 2. If you use a computer based spreadsheet, you may substitute a printout of your data for this table. Be sure to indicate that a spreadsheet is attached containing your data.

TABLE 2

ROOM TEMPERATURE: TEMPERATURE- °C

| BEAKER | %T | A | INITIAL $[Fe^{3+}]$ | INITIAL $[SCN^-]$ | EQUILIBRIUM $[Fe^{3+}]$ | EQUILIBRIUM $[SCN^-]$ | EQUILIBRIUM $[FeSCN^{2+}]$ | $K_c$ |
|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | |
| 2 | | | | | | | | |
| 3 | | | | | | | | |
| 4 | | | | | | | | |
| 5 | | | | | | | | |
| 6 | | | | | | | | |
| 7 | | | | | | | | |
| 8 | | | | | | | | |

COLD TEMPERATURE: TEMPERATURE- °C

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | | | | | | | | | |

HOT TEMPERATURE: TEMPERATURE- °C

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | | | | | | | | | |
| 8 | | | | | | | | | |

4. **CONCLUSION:** Compare your $\Delta H$, $\Delta G$ and $\Delta S$ with the following data from the CRC handbook (@ 298 K).

| | $\Delta H_f \left[\frac{KJ}{mol}\right]$ | $\Delta G_f \left[\frac{KJ}{mol}\right]$ | $\Delta S_f \left[\frac{KJ}{mol\ K}\right]$ |
|---|---|---|---|
| $SCN^-(aq)$ | 76.44 | 92.68 | .144 |
| $Fe^{3+}(aq)$ | -48.53 | -4.60 | -.316 |
| $FeSCN^{2+}(aq)$ | 23.43 | 71.13 | -.130 |

| | $\Delta H_{rxn}$ | $\Delta G_{rxn}$ | $\Delta S_{rxn}$ |
|---|---|---|---|
| Experimental | | | |
| CRC | | | |
| % Error | | | |

**Note:** These theoretical values will probably not match your experimental values very closely.

## INSTRUCTIONS FOR THE OPERATION OF THE SPEC 20

1. Be sure that the instrument is plugged in and turned on.

2. If the SPEC 20 is not on, turn it on by rotating the power knob on the left front face of the Spec 20, clockwise. It will then take 10 minutes to warm up.

3. Set the correct wavelength using the wavelength adjustment knob (on the upper face, right hand side of the instrument). The dial is calibrated in nanometers. Remember to interpolate between two scale markings to set the right wavelength. Ask your instructor if your not sure how to set it correctly.

4. Make sure that the sample compartment is empty and the cover closed. Adjust the power knob, still keeping the power on, so that the meter reads 0% transmittance.

**NOTE:** To avoid parallax error in your reading of the needle, move your head so that the needle and its reflection in the mirror, are superimposed.

5. Now fill the cuvette to the bottom of the frosted circle with de-ionized water. Wipe the outside of the cuvette with a tissue and make sure that it is free of fingerprints. Place the cuvette in the compartment making sure that the line on the cuvette is aligned with the line on the front of the sample compartment. Close the lid over the sample compartment.

6. Use the knob on the right front hand face of the Spec 20 to adjust the needle so that it reads 100% transmittance.

7. Repeat the above steps 4-6, until the Spec 20 is calibrated.

8. Make sure that the outside of the cuvette is clean and dry. The cuvette itself should be rinsed with a portion of the sample you wish to measure the percent transmittance of.

9. Fill the rinsed cuvette to the bottom of the frosted circle with the sample you wish to measure the percent transmittance of. Dry the exterior of the cuvette.

10. Place the cuvette in the sample compartment as before with the line on the cuvette aligned with the line on the front of the sample compartment.

11. Close the lid on the sample compartment and read the percent transmittance.

# ACID BASE TITRATION
## Chemistry 131

**INTRODUCTION**

Analysis of an unknown acid concentration is often determined by "titrating" the unknown acid with a known amount of base. In this experiment you will perform a titration of a strong acid (HCl) with a strong base (NaOH) and you will also perform a titration of a weak acid (acetic acid) with a strong base (NaOH).

**OBJECTIVE**

1. Understand the concept of the titration of weak and strong acids with a strong base.

2. Introduce the laboratory technique of titration.

**THEORY**

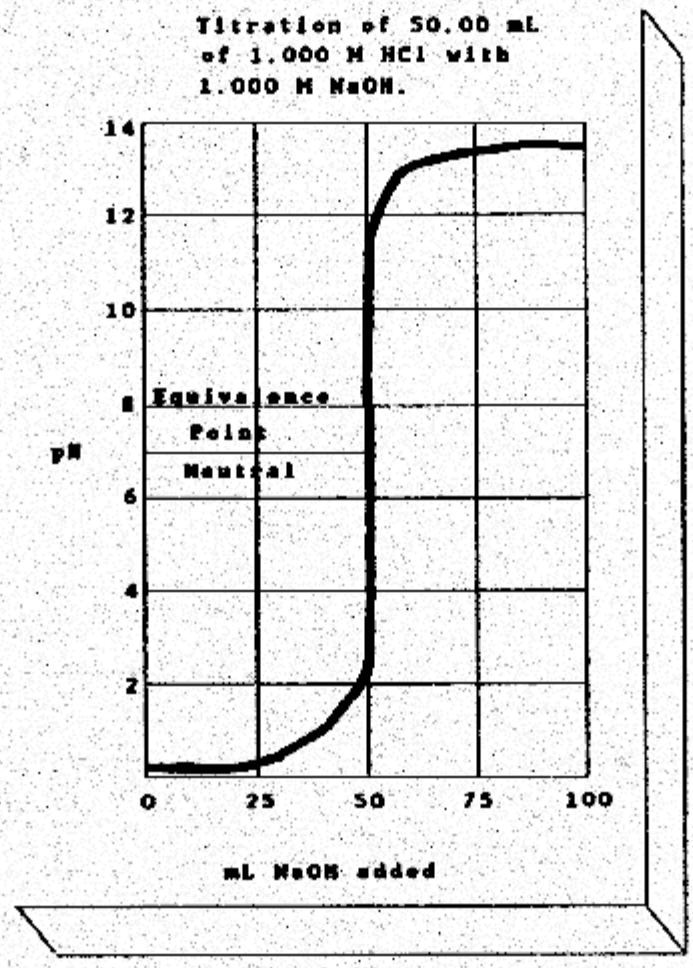
Refer to textbook for the complete theory of acid base titrations (Section 15.2; Chemistry, Masterton and Hurley). The following is a **brief** review of the theory.

The net ionic equation for the reaction between a strong acid and a strong base is as follows:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O \qquad (1)$$

The equilibrium constant for this reaction is approximately $10^{14}$, so that for all practical purposes this reaction goes to completion.

A typical strong acid/strong base titration curve is shown below. The volume of titrant is plotted versus the pH of the solution. The equivalence point on the titration curve represents the point at which the the moles of base (titrant) added is equivalent to the number of moles of acid in your unknown solution. Notice that the pH is 7 at the equivalence point for a strong acid/strong base titration.



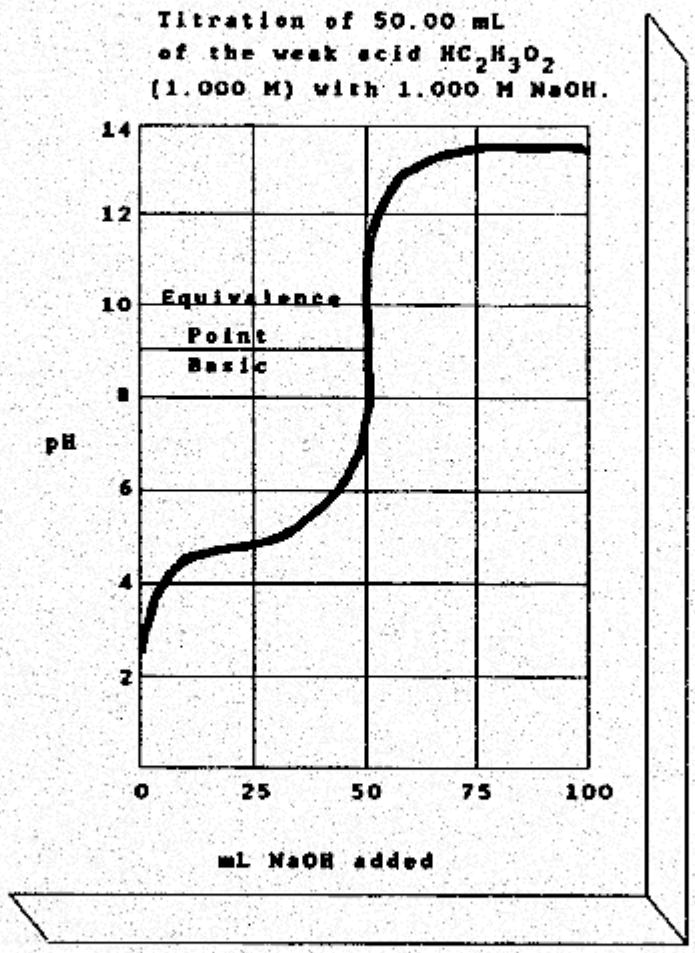

Since we will not know the pH of the solution in our strong acid/strong base titration, how can we determine the equivalence point? The answer is quite simple. We will use an indicator.

An indicator is just a very weak acid that changes color at different pH ranges. The indicator that we will use for the strong acid/strong base titration is phenolphthalein. Phenolphthalein changes from clear to red around pH 9. You may ask why are we using an indicator that changes color at pH 9 when the equivalence point occurs at pH 7. Notice that the titration curve is very steep both before and after the equivalence point. In fact, the line is almost vertical between pH 4 and pH 10. Because the line is vertical between pH 4 and pH 10, there is very little change in the volume of NaOH added in this range. Thus, any indicator that changes color in the vertical portion of the strong acid/strong base titration curve is acceptable.

A weak acid/strong base titration is quite different than a strong acid/strong base titration curve. Let's consider the titration of acetic acid with NaOH.

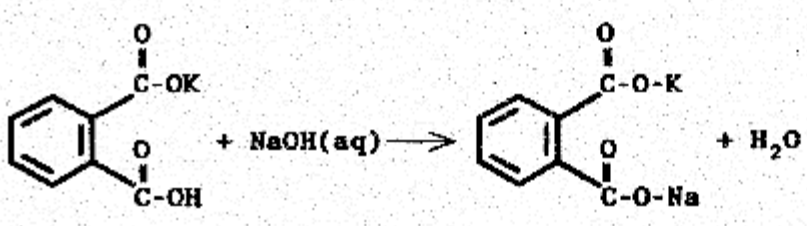
$$CH_3CO_2H(aq) + OH^-(aq) \longrightarrow CH_3CO_2^-(aq) + H_2O \qquad (2)$$

The equilibrium constant for this reaction is approximately $10^9$, so it too goes to completion. Let's consider how pH changes during the titration as shown in the following titration curve.




Notice that the pH starts at about 2.4 and rises rapidly. About halfway to the equivalence point the pH changes very slowly. In this region you have a buffer system--acetic acid and the acetate ions produced by that addition of $OH^-$ (as shown in equation 2). At the equivalence point the pH is greater than 7 because in this region there is no acetic acid left in solution, but only acetate ion, which is a weak base. Notice also that the curve is not nearly as vertical around the equivalence point as it was with a strong acid/strong base titration. Therefore, we must carefully choose an indicator which changes color very close to the equivalence point.

Before we start any titrations, however, a chemist needs to make sure that the concentration of the titrant is known exactly. The concentration of the sodium hydroxide solution may change with time. If $CO_2$ is absorbed by the NaOH solution, this would result in formation of carbonic acid which would neutralize some of the NaOH. To determine the exact concentration of the NaOH solution, therefore, we must "standardize" it against a known concentration of acid. The acid that we will use to standardize the NaOH is potassium hydrogen phthalate (KHP). It reacts with the NaOH according to the following reaction.




(3)

The procedure for standardizing the NaOH is to measure out a certain amount of KHP, dissolve it in water and titrate with NaOH to the equivalence point. Using the following relationship,

$$\text{Molarity}_{base} \cdot \text{Volume}_{base} = \text{moles of KHP} \qquad (4)$$

you can determine the exact molarity of the NaOH solution.

**PROCEDURE**

**(Note: Your instructor will direct you on the proper titration technique prior to performing the lab. If you have any questions please ask!)**

1. This lab will be conducted in pairs and written up independently. **All collaboration must be documented.**

2. Weigh 2 samples of approximately 0.4 grams of solid potassium hydrogen phthalate (KHP) and dissolve each in 50 mL of deionized water in a 200 or 250 mL Erlenmeyer flask. Add 5-6 drops of a 0.1 % phenophthalein indicator solution to each flask and then titrate the solution to a faint pink endpoint. Use these data to standardize the NaOH solution.

3. Once the NaOH solution is standardized, determine the molarity of an unknown hydrochloric acid solution by titrating approximately 10 mL of the unknown acid with the standardized NaOH solution. Perform two replicates using a phenolphthalein endpoint.

4. Determine the molarity of an unknown acetic acid solution by titrating approximately 10 mL of the unknown with NaOH to a

phenolphthalein endpoint. Perform two replicates with the phenolphthalein indicator.

5. Next titrate the same unknown acetic acid solution using methyl orange as an indicator. Perform the titration only once.

6. Your instructor will direct the entire class to perform a pH titration of the unknown acetic acid solution using NaOH and no indicator. The data from this titration will be supplied to the whole class. The procedure for the pH titration is as follows:

a. Measure the pH of the solution before adding titrant.

b. Add a small volume of titrant. Stop, record volume added, measure and record the pH.

c. Repeat step "b" until within about 2.0 mL of the equivalence point or use volume increments that give approximately 0.2-0.3 pH unit changes.

d. In the vicinity of the equivalence point, many data points are needed, so take pH readings after every 0.10 mL titrant is added.

e. After the equivalence point, continue taking readings (at 1-2 mL increments) until at least 5 mL beyond the equivalence point.

**DATA**

**CONCLUSIONS (Show all calculations)**

1. What is the average molarity of the NaOH solution?

2. What is the average molarity of the unknown HCl solution?

3. What is the average molarity of the unknown acetic acid solution using phenolphthalein as an indicator?

4. What is the molarity of the unknown acetic acid solution using the methyl orange indicator? Is it different than the titration using the phenolphthalein endpoint? If so, why?

5. Plot the pH titration data of the unknown acetic acid with NaOH using Quattro. (Attach the graph to this lab also!)

a. What is the equivalence point in mL NaOH? (Mark it on the graph also.)

b. What is the pH half way to the equivalence point?

c. What is the pH of the solution at the equivalence point?

d. What is the effective pH range of phenolphthalein as an indicator? (Highlight this range on the graph.)

e. What is the effective pH range of methyl orange as an indicator? (Highlight this range on the graph also.)

**PRELAB EXERCISE**

1. Draw a typical weak acid strong base titration curve. Label the axes and equivalence point.

2. Define equivalence point.

3a. What is the pH of a 1.00L 0.1 M acetic acid solution?

b. What is the pH of the above solution after the addition of 500 mL of 0.1 M NaOH solution?

c. What is the pH of the above solution after it has been titrated with 0.1 M NaOH to its equivalence point?

d. What is the pH of the above solution after addition of 1.01 L of .1 M NaOH?

# PHOTOGRAPHY
## Chemistry 131

### Introduction

The following appeared in the Gazette de France on 6 January 1839: "An important discovery by our famous painter of the Diorama, M. Daguerre. The discovery partakes of the prodigious. It upsets all scientific theories of light and optics, and will revolutionize the art of drawing." The author was describing a paper presented by Daguerre at the National Academy of Science on how light was used to "make" pictures. This was the start of photography.

Photography is a true blend of art and science. In its beginning a photographer was more scientist and experimenter than artist. He had to prepare his film and development procedures from scratch. There were no off-the-shelf film or 24 hour development labs. Every part of photography was done by the photographer. Today modern science and technology provide us with very sophisticated cameras and film capable of recording images and detail as never before. But high technology is only a beginning for good photographs. Juxtaposition of subject elements, perspective, light and shadows--these are the things the photographer must apply artistic talent in order to create superior photographs. Today we will not be concerned about photo quality. Instead we will concern ourselves primarily about the chemistry of photography.

### Objective

1. To understand the chemical principles involved in photographic paper development.

2. Reinforce the principles of acid base reactions, precipitation reactions, oxidation reduction reactions and equilibrium.

### Theory[1]

The basic principle of photography is that light is focused on photographic paper containing silver halides. This light forms an invisible image called a "latent image". The latent image process is just a very simple oxidation reduction reaction. First the halide ($Cl^-$, $Br^-$ or $I^-$) absorbs a photon of light ($h\nu$) and releases an electron in an oxidation reaction (1). The electron released from the halide reduces the silver ions to form metallic silver (2). This metallic silver is the basis of the latent image.

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1. *Bunting, Roger; The Chemistry of Photography; 1987;* (Portions of the theory copied with permission of Professor Bunting.)

$$\text{light } (h\nu) + Br^- \text{ -----> } Br + e^- \qquad (1)$$

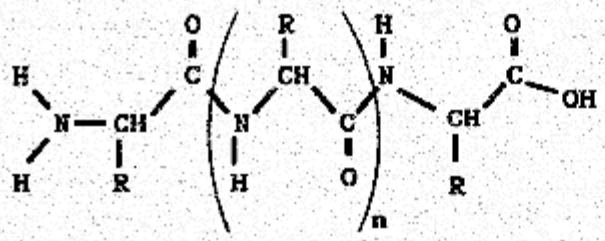
$$Ag^+ + e^- \text{ -----> } Ag(s) \qquad (2)$$

This latent image is magnified during the development process via a number of chemical reactions and the result is a negative photograph. The magnified image on the photo paper appears opposite that of the real object. That is the light parts of the object appear dark and the dark parts of the object appear light. The reason for this is that the reduced silver on the photo paper is formed in very small, evenly dispersed particles. When light hits the reduced silver, the small particles diffract the light and make it appear dark. The unexposed portion of the photo paper corresponds to the dark parts of the object. However, since there is no unreduced silver particles on the unexposed photo paper this region appears light. The chemistry of the negative development process is described below.

**Photographic Paper**

The essence of photographic paper is a layer of silver halide (AgCl, AgBr, and AgI) on a clear plastic support. The silver halide, principally bromide, is a fine powder and must be somehow fixed to the surface of the plastic base. The material used to bind the silver halide to this support must be transparent to allow light to reach the silver halide grains; it must be fairly rigid to prevent particle movement which would blur the image; yet it must not be brittle so as to crack when the film is flexed. Finally, and of utmost importance, it must allow water and solutions to penetrate it so that the reacting chemicals may reach the silver halide in the processing steps.

The material which meets all of these requirements is the same as that used in fruit flavored "jello" desserts---gelatin. Gelatin is a very complex and indefinite molecular structure. It is a protein material and is made up of amino acids. These molecules are typically made up of long chains of 300 to 900 atoms (where n = 100-300) as shown in the following figure.



(3)

The symbol R is shown to represent some group of carbon atoms of unspecified length or structure. In proteins these R groups may contain occasional atoms of nitrogen, oxygen, sulfur or phosphorous. The composition of these R groups have a profound effect on the properties of the film. For this lab we will not discuss any of those effects.

Now let's consider the preparation of the silver halide, which must be suspended in the gelatin. One way to form it would be to react silver with bromine to form silver bromide according to the following.

$$2Ag(s) + Br_2(\ell) \text{ -----> } 2AgBr(s) \qquad (4)$$

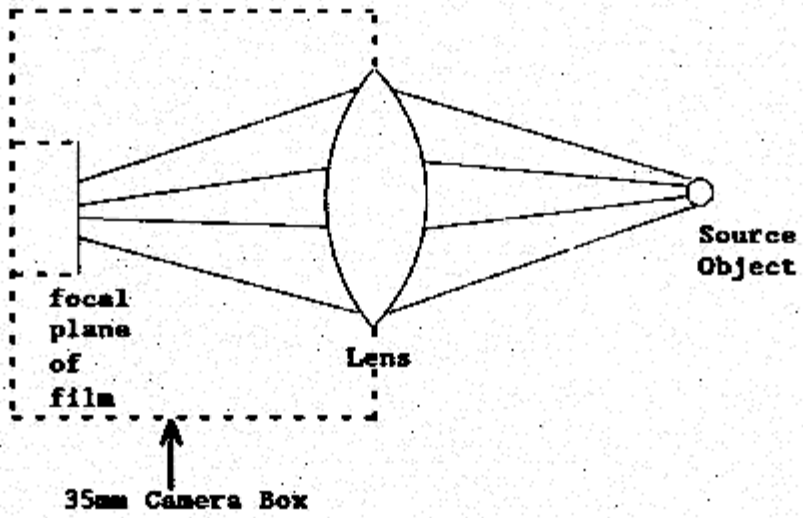
If we drop a chunk of silver into bromine liquid we will only form AgBr on the "outside" of the chunk. For the purpose of film, this is not an acceptable way to incorporate AgBr in the gelatin. Recalling your solubility rules, a better procedure would be to take a solution of $AgNO_3$ and mix some KBr solution with it. The reaction is as follows

$$AgNO_3(aq) + KBr(aq) \text{ -----> } AgBr(s) + KNO_3(aq) \qquad (5)$$

Commercially the procedure for making film is to take $AgNO_3$ and mix it with various halide salts (KBr, KI, KCl) in a liquid gelatin at a temperature of 50-80° C for 1-2 hours. (The KI and KCl is used to vary film sensitivity and grain size.) The solution is quick chilled, solidified, shredded and washed to remove the KBr, KI, and KCl. Finally it is remelted and spread on a film or photographic paper in a very thin and precisely uniform layer.

## Optics

In a typical 35 mm camera, the image if focused through a lens as shown in the following diagram.

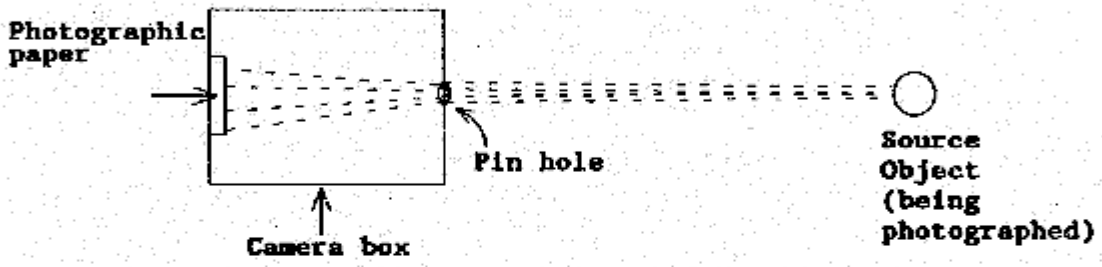


Camera lens normally contain a diaphragm--a device to provide a circular hole of variable diameter. The diaphragm is known as the aperture and its principle function is to control the intensity of light which passes through the lens to the film. Adjusting the "f-stop" or "f-number" on a camera lens is just making a variation in the aperture diameter. The f-number is equal to

$$\text{f-number} = \text{focal length/aperture diameter} \qquad (6)$$

As you can see, for a camera with a fixed focal length, the smaller the f-number the larger the aperture diameter. The other adjustable settings on a camera is the shutter speed. The faster the shutter speed, the less light reaches the film and the slower the shutter speed, the more light reaches the film.

With our pin-hole cameras, the optics are very simple. The camera has no lens, but has a pin hole which allows light to enter in and expose the film.




To vary the amount of light that reaches the photographic paper there are only two controls:

1. Size of the hole.
2. Length of time film is exposed.

The specifics of hole size and film exposure time is discussed in procedure section.

**Developing the Image**

In order to produce a visible image on an exposed film, additional silver must be deposited in the vicinity of each of the small silver specks that make up the latent image. This is brought about by the development process.

Photographic developers contain chemicals that are reducing agents. These reducing agents readily give up electrons to reduce the silver ions in the silver halide to metallic silver.

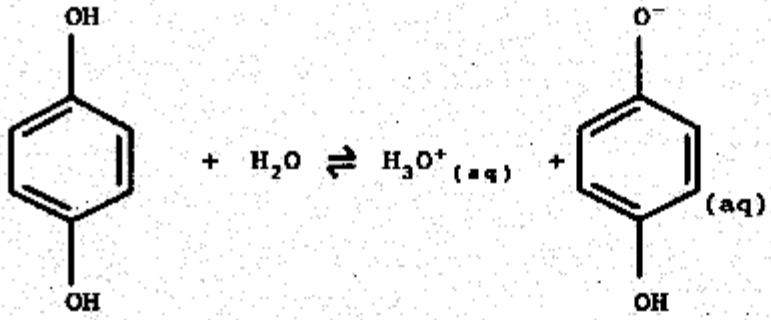
What sort of materials can serve as developing agents? A logical guess would be some other metal more active than silver. A metal that is "more active" is one that can give up its electrons more readily than silver (i.e., has a higher oxidation potential). Mercury is an example. It is slightly more active than silver, and so can react with a silver halide as the following equation shows:

$$Hg(l) + AgBr(s) \longrightarrow HgBr(s) + Ag(s) \qquad (7)$$

Bromide is just a spectator ion and it remains unchanged through the process.

Mercury metal once was used as a developing agent in just this manner. Its effects were discovered quite accidentally by Daguerre in 1835. Daguerre prepared silver iodide emulsions, exposed them in a camera and then stored the exposed plates near some spilled mercury from a broken thermometer. The result was that the mercury developed his exposed film (containing a latent image) into a visible image. These photographs later became known as "daguerrotypes."

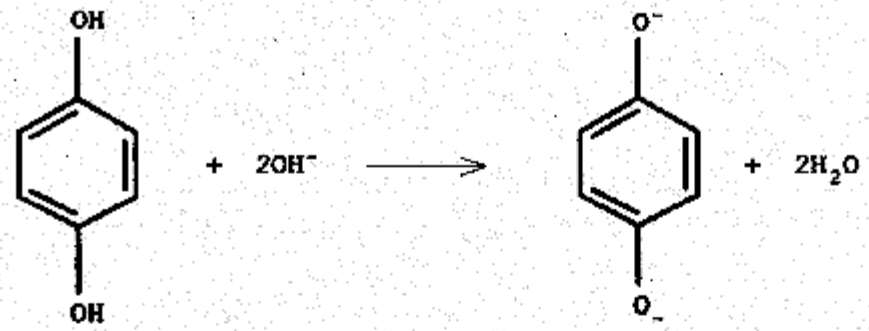
The reducing agents in developers in use today are all organic compounds soluble in water. In solution the molecules have the necessary mobility to get in contact with the insoluble silver halide in order to reduce the silver in the film emulsion. The most widely used reducing agent in photography today is hydroquinone $C_6H_4(OH)_2$. Hydroquinone is a weak acid that dissociates according to the following reaction:




(8)

Since this equilibrium lies far to the left we must add a chemical in order to "activate" hydroquinone. The chemical which activates hydroquinone is hydroxide. When a base is added the hydroxide reacts with the two protons on hydroquinone to form the

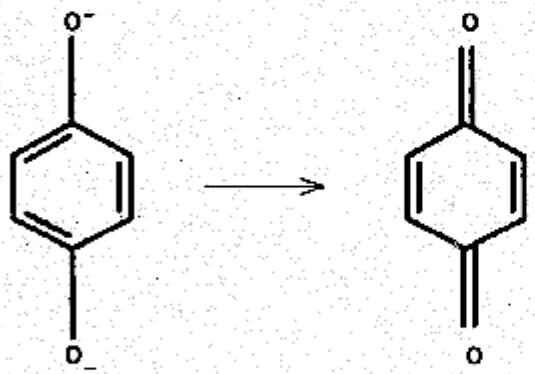
dianion of hydroquinone according to the following reaction:




(hydroquinone) (hydroquinone dianion) (9)

In the presence of $Ag^+$,  acts as a reducing agent and

becomes oxidized according to the following half reactions:

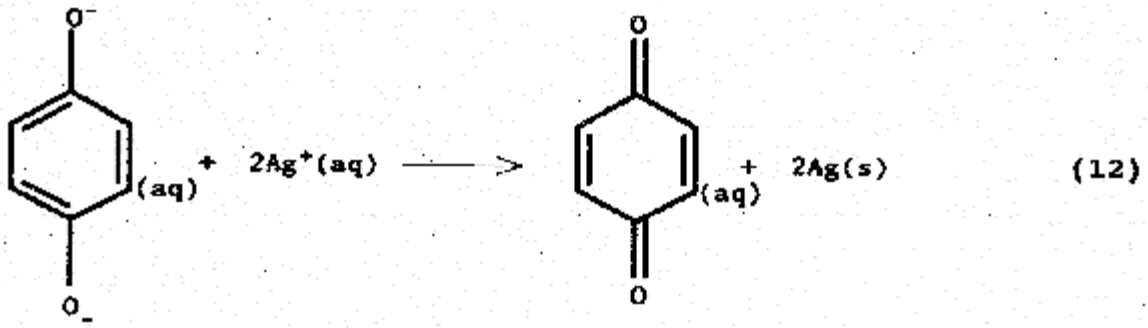



(10)

(hydroquinone dianion) (quinone)

$Ag^+(aq) + e^- \text{-----> } Ag(s)$ (reduction half reaction) (11)

Thus the overall reaction is:




(12)

The pH range of all developer solutions is always basic. Normally the pH range is 10-12 using $Na_2CO_3$ as the base.

Up to this point we have ignored an obvious question regarding the development reaction. Why is it that the reduction of silver in the emulsion occurs only in the vicinity of the silver particles of the latent image? Why aren't all the silver ions reduced? The answer to this question is that the rate of reaction of the silver near the latent image is much greater than the rate of reaction of silver <u>not</u> near the latent image. The developer can and will reduce all the silver ions in the film and if development is extended for too long a time the entire emulsion will turn black. The reason we can use the development reaction to produce an image is that reduction occurs faster near the silver particles. So we can develop a film or print until the image sufficiently darkens, but stop the development before the slower reacting silver halide is reduced. The silver metal of the latent image acts as a catalyst for reduction of the silver ions with which it is in contact. Chemical development would not be possible if it were not for this catalyst.

**Stop Bath**

When the development process is completed - that is when sufficient silver has been reduced to give the desired image density - the film is placed into a stop bath. The purpose of the stop bath is to prevent any further reduction of silver ions. Since the developer solution is only activated at pH ranges above 7, then one way to stop the development process is to "wash" the film in an acidic bath and in so doing shift the equilibrium of the developer solution from quinone to hydroquinone.

By adding acid, the $H^+$ will react with the excess $OH^-$ in the developer to form water. Since there is no hydroxide to "activate" the hydroquinone, development can not occur.

**Fixer**

After the reaction is stopped, we are left with a silver image superimposed on a background of pale yellow silver halide. This silver halide which was not reduced in development must be removed by the fixing process. If not, a print would ultimately darken due to gradual reduction of more silver from exposure to light. Fixing is a process by which the remaihing insoluble silver halide is converted to a soluble material which can be washed out of the emulsion. A great many substances, both negative ions and neutral molecules, have since been found which will complex silver ions. Ammonia, for example, is a molecule that can dissolve silver chloride by bonding to it to produce a complex positive ion.

$$AgCl(s) + 2NH_3(aq) \text{ -----> } Ag(NH_3)_2^+(aq) + Cl^-(aq) \quad (13)$$

The materials commonly used in photographic fixing solutions today are salts containing the thiosulfate ion $S_2O_3^{2-}$. The fixer used in this lab is ammonium thiosulfate or $(NH_4)_2S_2O_3$. The fixing action of thiosulfate on silver bromide is as follows:

$$AgBr(s) + 2S_2O_3^{2-}(aq) \text{ -----> } Ag(S_2O_3)_2^{3-}(aq) + Br^- \quad (14)$$

Thiosulfate dissolves the silver bromide and the ammonium ion can dissolve the silver chloride.

$$AgCl(s) + 2NH_4^+(aq) \text{ -----> } Ag(NH_3)_2^+(aq) + 2H^+(aq) + Cl^-(aq) \quad (15)$$

Developing, stopping, and fixing are the three sequential steps that must be performed in the standard processing of all black and white photographic materials. Following these three steps it is necessary to thoroughly rinse a film or print before drying. If any thiosulfate is left in the emulsion the image will not be permanent. Excess thiosulfate in the emulsion will turn the photo yellow and eventually cause the image to fade.

**Reversal Processing**

In order to obtain a positive image, the reversal process is used. Recall that the latent image is made of reduced silver and appears dark, even though that it represents the "light" part of the object. The unreduced silver on the photo paper appears light and represents the "dark" part of the object. In order to reverse this, the latent image is bleached and washed out, and the unreduced silver is exposed to light. This produces a photo in which light parts appear light and dark parts appear dark.

The procedure for this is quite simple. The photo paper is placed into the developer and left there until the latent image is formed. The paper is then placed into a bleach bath of potassium dichromate to oxidize the silver from the latent image. The photographic paper is washed to remove the bleach and the dissolved (oxidized) silver, and then exposed to light so the remaining silver halide forms the positive latent image. The photo paper is then developed, washed, rinsed and dried.

**Procedure**

1. Build a pin hole camera. If you have any questions about the construction, see your instructor. Cut a 1 cm x 1 cm hole in the side of the box. On the inside of the box, tape a piece of aluminum foil over the hole. With a paper clip punch a hole (the smallest hole possible) in the foil. On the outside of the box, cover the hole with electrical tape. Under safe light conditions, insert the photographic paper into your box and tape it against the inside of the box directly opposite the pin hole. Tape the box shut so that it is light tight.

2. Expose the paper to your subject for approximately 1 second (on a sunny day) and for 3-5 seconds (on a cloudy day). The sun must be to your back to avoid overexposing the paper.

3. Under safelight conditions, develop your photographic paper. For negative processing, place the paper into the developer. Gently agitate the paper while it is submerged in the developer. When your image begins to appear remove the paper. Some development will occur after the paper has been removed from the developer. When the image is developed, place the paper in the acid stop bath for about 1 minute. Next, place the paper in the ammonium thiosulfate $(NH_4)_2S_2O_3$ fixer for about a minute. Rinse the paper completely with tap water and allow to dry.

4. For reversal processing, place the paper in the developer. Gently agitate the paper while it is submerged in the developer and slightly overdevelop your image. Place the paper in the $K_2Cr_2O_7$ bleaching solution. Your image will disappear as all of the metallic Ag is dissolved. Rinse your paper and turn on the lights. Place the paper back into the developer and the positive image will appear. Rinse the paper completely and allow to dry.

**Conclusions**

1. What is the pH of a 0.1 M hydroquinone solution (Ka = $4.5 \times 10^{-11}$)?

2. What "activates" hydroquinone to be a developing solution?

3. Typically hydroquinone is placed in $Na_2CO_3$ buffer solution. What is the pH of a buffer solution containing 0.15 M $Na_2CO_3$ and 0.10 M $H_2CO_3$? If the effective pH range for hydroquinone development solution is 11.0 or greater, would the above buffer be adequate?

4. For $Br^-$ to be oxidized to Br requires a photon with an energy of at least $2.58 \times 10^{19}$ J. What wavelength of electromagnetic radiation does this correspond? If the safelight emits in the red region at 750 nm, would the safelight effect the photo paper?

5. During negative processing, why must photo paper be placed in the "fixer"?

6a. Given that $[Ag^+] = 0.0025$ M in a 4 liters of spent fixing solution, how many grams of silver is in the solution?

6b. How many grams of NaCl should be added to the solution to reduce the $[Ag^+]$ to $1.0 \times 10^{-6}$ M?

6c. How much silver was recovered in this process?

7. Explain why the developer reduces silver around the latent image and not in the unexposed areas.

8a. Potassium dichromate is used to bleach out (oxidize) the silver from the latent image in reversal processing. The following represents the overall unbalanced redox equation. Balance the equation.

$$Ag(s) + K_2Cr_2O_7(aq) + H_2SO_4(aq) \text{ -----> } Ag_2SO_4(aq) + Cr_2(SO_4)_3(aq) + K_2SO_4(aq)$$

8b. When the bleaching solution becomes "weak" a small amount of sulfuric acid is added. Why?

9. What is the result of overexposed photo paper?

10. Attach your photo to the lab. What could you have done during this lab to improve your photo?

## Prelaboratory Exercise

1. How does light expose black and white photo paper? (Include chemical equations.)

2. Why does reduced silver appear black on photo paper?

3. If $Br^-$ was oxidized to $Br_2$ instead of just Br, what effect might that have on the formation of latent image.

4. Why is gelatin used as the matrix for silver halide?

5. Why is acetic acid used in the stop bath?

# QUALITATIVE ANALYSIS
# IDENTIFICATION OF CHEMICAL COMPOUNDS
# Chemistry 131

## INTRODUCTION

Qualitative analysis is the process of identifying the content of a sample with regard to the chemical species present. No assessment of the amount of the chemicals present is required.

This lab is the culmination of your chemistry experience for the semester. You have learned about chemical reactions and the behavior of chemical species, the properties of solutions, complex ions, and solids. Now you must integrate all these concepts, selectively using each tool of knowledge to analyze qualitatively unknown chemical samples.

## OBJECTIVES

Your goal in this lab is to successfully identify the cation and anion in five separate unknowns. You will do this in two parts. The first part of the lab consists of creating a "reaction matrix" by mixing known chemicals and observing and recording the product of any reaction. In the second part, you will identify the unknowns. You will be required to perform the second part without any collaboration from any source except your written notes from your reaction matrix, your knowledge of chemistry, and this laboratory handout.

## THEORY

Ions in solution (whether cation or anion) have distinctive properties which allow them to be identified by controlling the experimental conditions. Certain ions form precipitates based on the solubility product constant, Ksp, of any resulting species formed. Others may undergo oxidation-reduction reactions that produce gases (visible as bubbles in solution) or changes in color of the solution. Some ions form complex ions with distinctive colors. Finally, some ions react with the water to result in either basic or acidic solutions. You have observed all these chemical characteristics in previous labs and as demonstrations during this semester.

Salts are compounds that are made from cations and anions. In solution, these ions dissociate into individual species that possess unique characteristics. First, let's practice with the ions produced by salts. Below is a table of six salts and the resulting ions produced. Complete the table by filling in the blanks:

| Salt | Cations | Anions |
|---|---|---|
| $AgCl$ | | |
| $NH_4NO_3$ | $Ba^{2+}$ | $F^-$ |
| $FeSO_4$ | $Ba^{2+}$ | $PO_4^{3-}$ |
| $ZnS$ | | |

Remember that an ion may have various oxidation states, but the overall charge on the neutral salt must equal zero.

A proven way of approaching this problem is to first identify the cation in an unknown. Four "stock" reagents will be provided that give distinctive information about the cation. They are ammonium hydroxide, hydrochloric acid, sodium hydroxide, and potassium permanganate. Once the cation is positively identified, the anion is identified by performing similar tests. You will also use twelve different salts that contain all the cations you will see in the unknowns. Reacting the salts together provides a data base of observation to correctly identify the cation. It is crucial that you record detailed observations of the salt reactions.

An obvious fact that is often overlooked is that the sample compound must be water soluble. If not, you would observe a solid in your unknown. Using the solubility rules narrows your investigation by reducing the range of possible compounds.

**Sample Analysis**

Let's work through a sample qualitative analysis. Our unknown is a clear, colorless liquid. Mixing with a drop of hydrochloric acid gives a white precipitate, as does mixing with a drop of sodium hydroxide and ammonium hydroxide. Potassium permanganate produces no observable change.

A positive reaction with hydrochloric acid may indicate the presence of a base; but our unknown also reacts with the bases sodium hydroxide and ammonium hydroxide. Since a white precipitate forms, let's refer to the solubility rules for help.

**RULE 1: All nitrates ($NO_3^-$) are soluble.**

Our unknown is soluble - it may be a nitrate. However, none of the precipitates formed are nitrates.

**RULE 2: All chlorides, bromides, and iodides are soluble EXCEPT those of silver, mercury(I), and lead. Copper iodide is also insoluble.**

Our unknown could be one of the soluble halides. But, the addition of chloride (from the HCl) resulted in formation of a precipitate. Thus, our cation is either silver, mercury, or lead.

**RULE 3: All sulfates ($SO_4^{2-}$) are soluble except lead, strontium, barium, calcium, and mercury(II). Silver sulfate is sparingly soluble.**

Our unknown could again be a soluble sulfate. However, since we have already limited our choice of cations to silver, mercury(I) and lead, we can rule out lead sulfate and probably silver sulfate.

**RULE 4: All carbonates ($CO_3^{2-}$), phosphates ($PO_4^{3-}$), and chromates ($CrO_4^{2-}$) are insoluble except the alkali metals and ammonium.**

Little here except that the cation could be an alkali metal or ammonium but we already know it is not.

**RULE 5: All hydroxides ($OH^-$) and sulfides ($S^{2-}$) are insoluble except the alkali metals and ammonium. Calcium and barium sulfides hydrolyze in water to form hydroxides.**

Our unknown formed a solid with hydroxide ($NH_4OH$ and NaOH). Once again, the cation cannot be an alkali metal or ammonium.

Based on these tests, we have narrowed our cation to three possible ions: lead, silver, and mercury(I). We need more data.

By reacting this unknown with our four other unknowns, we can build a smaller reaction matrix similar to the one you will build in Part A. Now the detailed observations of that reaction matrix are used. We notice that one of the reactions is similar to that between sodium iodide and lead(II) nitrate, forming the yellow precipitate, Lead (II) iodide. Since mercury is not included in the reaction matrix, we eliminate it as a possibility. Silver does not give a yellow precipitate with iodide. We now can assign our first cation as lead(II).

Having identified our cation as $Pb^{2+}$, we now pursue the anion.

Using a similar method of deductive reasoning and elimination, the anion is identified as nitrate, $NO_3^-$. (It is the only anion in the reaction matrix with which lead is soluble.)

## EXPERIMENTAL

### A. REACTION MATRIX

In the first part of this lab you'll develop a reaction matrix by reacting several salt solutions with four standard reagents (the stock solutions): HCl, NaOH, $NH_4OH$, and $KMnO_4$. You'll also react each salt solution with all the other salt solutions.

1. Place 12 drops of each stock solution on the acetate reaction surface. You should lay out these solutions to mimic the Reaction Matrix on page 7, making the collection of data easier.

2. Add one drop of each salt solution to a separate drop of stock solution. Carefully record your observations on the Reaction Matrix. Pay careful attention to color, general appearance, reaction times, bubbles, etc. You will use only observations for determination of the unknowns in Part B.

3. Now complete the Reaction Matrix by reacting one drop of each salt with a drop of all the other salts. Again, carefully observe and record any changes that occur.

4. For each mixture which reacts, you should be able to identify what occurred. For example, mixing $AgNO_3$ and NaCl produces a white precipitate; you should be able to identify the precipitate as AgCl. Silver chloride should form when any soluble silver compound and soluble chloride compound are mixed. Identify reaction products on the Reaction Matrix wherever possible.

5. Using a similar methodology, you should be able to identify any precipitation reactions that are not predicted, or expected, using the solubility rules. Carefully look over your Reaction Matrix. Note below any precipitation reaction that the solubility rules would not predict:

6. Now check the table for any precipitation reaction that you would have predicted based on the solubility rules that did not occur. Record these below (show the expected precipitate as well as reactants):

7. After making all observations, clean your reaction surface and return the salt solutions to their appropriate trays. Keep the four stock solutions.

**B. IDENTIFICATION OF UNKNOWNS**

1. Ask your instructor for your five unknown solutions.

a. From this moment forward, you are not allowed any collaboration with any source. Do not talk to your classmates. Do not consult any textbooks or notes except those you have written in this lab handout. Your instructor will discuss the chemistry of reactions of compounds, but will not be able to answer any questions concerning identifying the unknowns.

b. Your unknowns are not necessarily the same salts as you used in Part A. However, only the ions in Part A are contained in these unknowns, making 9 possible cations ($Al^{3+}$, $Ba^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Fe^{2+}$, $Pb^{2+}$, $Mn^{2+}$, $Ag^{+}$, $Na^{+}$) and 5 possible anions ($NO_3^{-}$, $SO_4^{2-}$, $CO_3^{2-}$, $Cl^{-}$, and $I^{-}$).

c. Make initial observation concerning these five unknowns. Record the numbers on each microburet which identifies the unknown on the Unknown Reaction Matrix (pg 8). Carefully record below the physical characteristics of your unknowns (color, presence of precipitate, etc.):

**UNKNOWN #1:**

**UNKNOWN #2:**

**UNKNOWN #3:**

**UNKNOWN #4:**

**UNKNOWN #5:**

2. React each unknown with the four stock solutions and record any observations on the Unknown Reaction Matrix.

3. React the five unknowns together, again recording your observations on the Unknown Reaction Matrix.

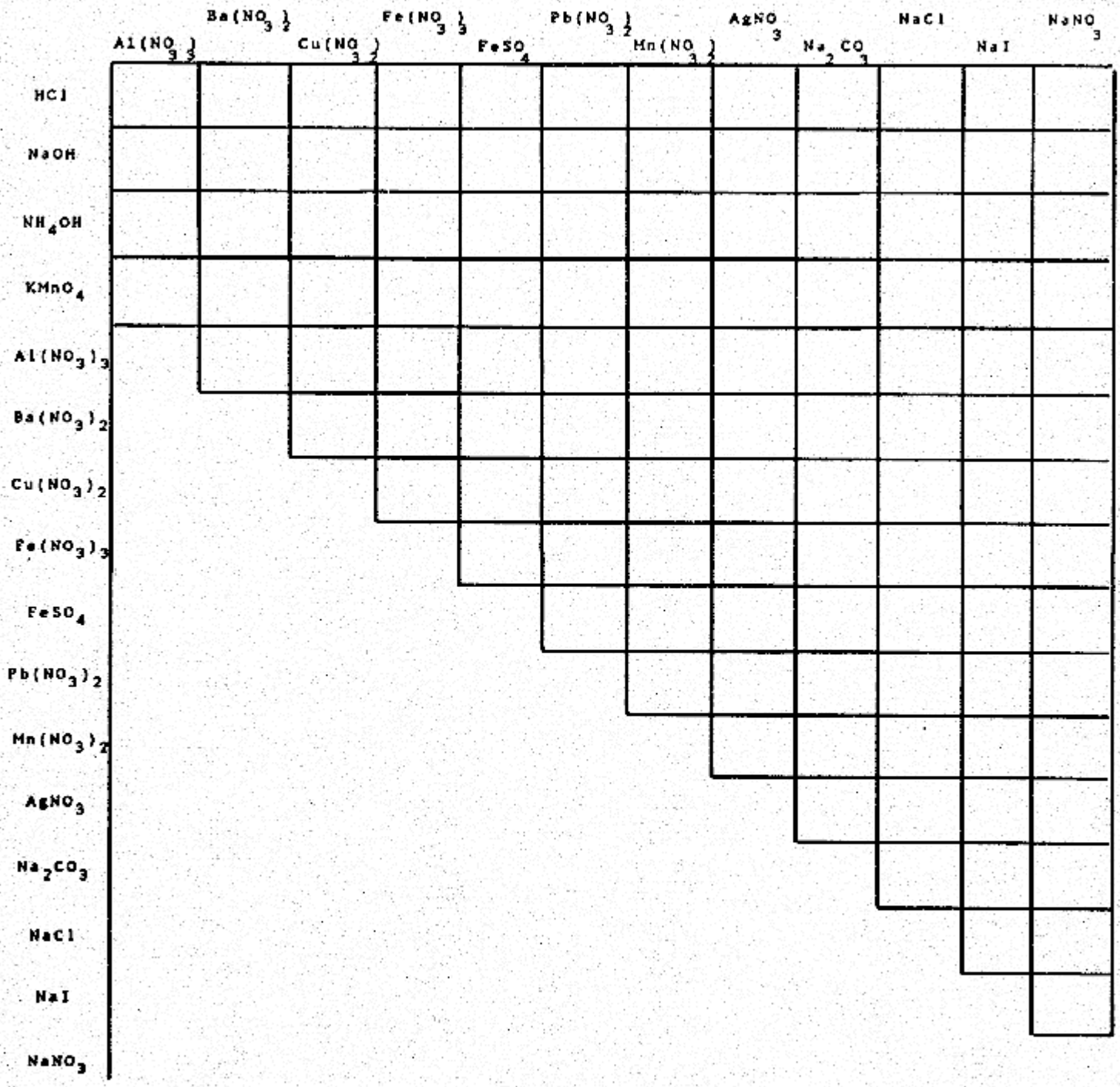
4. Using the data you gathered in the first part, your knowledge of chemistry, solubility rules, etc., identify the ions present in your unknowns. Each unknown contains only one cation and one anion.

a. THINK!! Ask yourself if the combination of ions is reasonable. For example, could AgCl be one of your unknown solutions? A quick review of the solubility rules will answer this one.

b. RELAX!! Use a process of elimination to narrow your possible ions.

Your analysis and identification of the five unknowns (ten total ions) must be completed prior to the end of the laboratory period. Your grade for this lab will be based on correctly identifying the ten unknown ions, each worth ten points (100 points total for the lab). NO OTHER WORK IS REQUIRED.

## REACTION MATRIX (PART A)

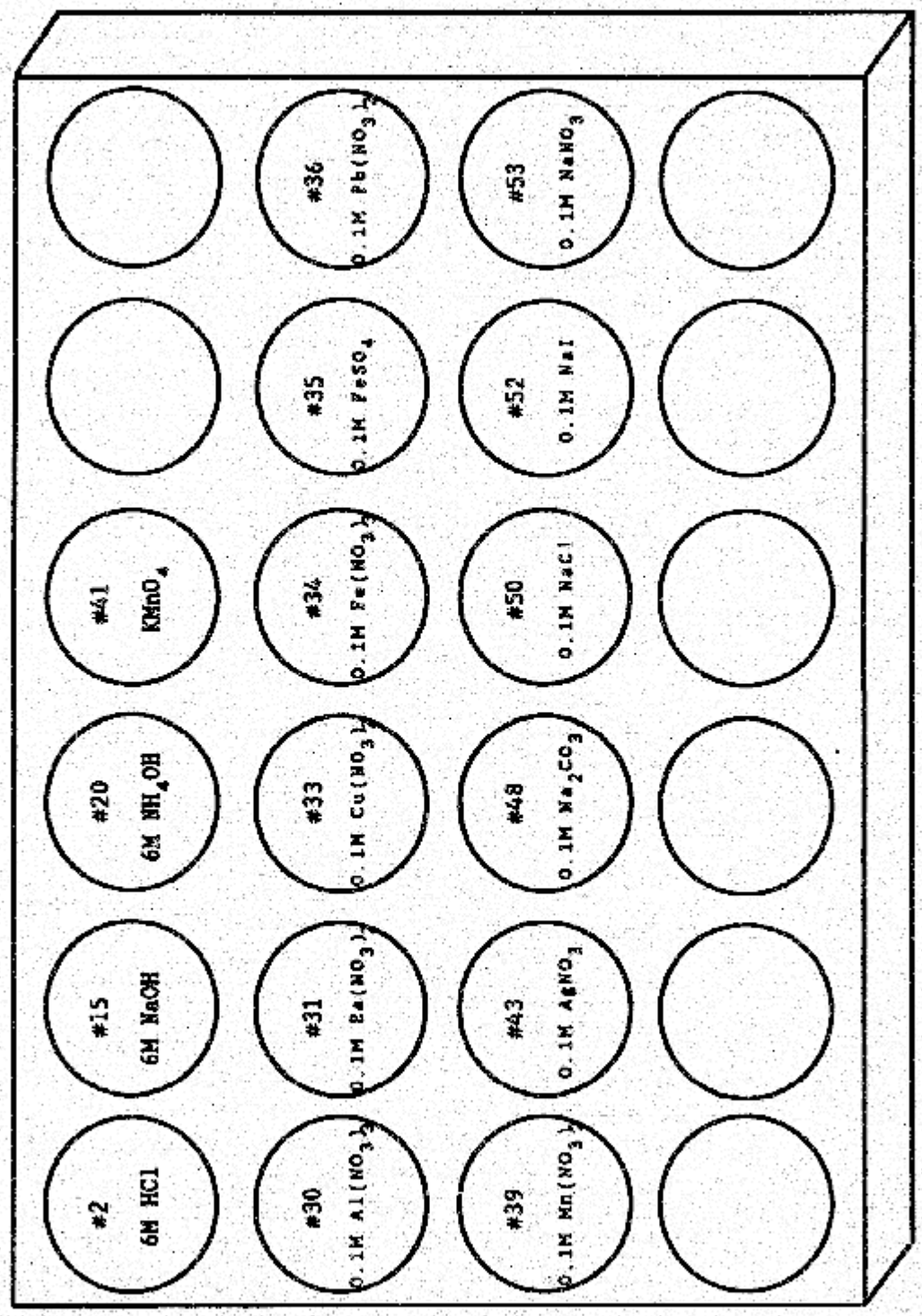


## UNKNOWN REACTION MATRIX (PART B)

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | | | | | |
| HCl | | | | | |
| NaOH | | | | | |
| $NH_4OH$ | | | | | |
| $KMnO_4$ | | | | | |

UNKNOWN LETTER ____ RESULTS

| | | | | | |
|---|---|---|---|---|---|
| UNKNOWN NUMBER | | | | | |
| CATION | | | | | |
| ANION | | | | | |


#2
6M HCl
#15
6M NaOH
#20
6M $NH_4OH$
#41
$KMnO_4$
#30
0.1M $Al(NO_3)_3$
#31
0.1M $Ba(NO_3)_2$
#33
0.1M $Cu(NO_3)_2$
#34
0.1M $Fe(NO_3)_3$
#39
0.1M $Mn(NO_3)_2$
#43
0.1M $AgNO_3$
#48
0.1M $Na_2CO_3$
#50
0.1M NaCl
#35
0.1M $FeSO_4$
#36
0.1M $Pb(NO_3)_2$
#52
0.1M NaI
#53
0.1M $NaNO_3$

153

# CHEMICAL KINETICS
## Chemistry 131

## INTRODUCTION

We may ask four basic questions about a chemical process. First, is the reaction spontaneous? Thermodynamics allows us to determine the conditions under which spontaneity occurs. Second, how fast will the reaction proceed? Third, what is the "sequence" of forming the products? Chemical kinetics provides answers to how fast and gives insight to the reaction mechanism. Lastly, how far will the reaction go before reaching a state of equilibrium? Study of the equilibrium constant, $K_{eq}$, may answer this question. You have studied thermodynamics and equilibria in previous labs. Now let's take a look, at the *kinetics* of a reaction.

Kinetics is important because it allows us to determine the rate of the reaction. Experiments have shown that the rate of a chemical reaction is dependent on several factors. The four most important are: (1) nature of the reactants, (2) concentration of the reactants, (3) temperature, and (4) catalysts.

The purpose of this experiment is to examine the effects of these factors on a chemical reaction. In the first experiment, you will observe the effects of concentration by reacting various concentrations of hydrochloric acid with zinc and aluminum metal. To observe the effect of temperature, you will repeat the experiments on ice cubes.

In the second part of the lab, you will study the reaction of hydrogen peroxide and iodide in acidic solution:

$$H_2O_2 + 2H^+ + 3I^- \longrightarrow I_3^- + 2H_2O \qquad (1)$$

You will observe the effects of the change of reactant concentrations to determine the rate law of the reaction. From the rate law, we will make predictions concerning the mechanism by which the products are formed.

### REACTION RATES

We can quantitatively express the rate of a reaction in terms of rates of change in concentration of the chemical species present in the reaction. This change is either written in terms of the *disappearance of a reactant* or the *appearance* of a product. For example, the famous reaction of A and B to form C could have the rate expressed three ways. Two of these ways are:

$$A + B \longrightarrow C$$

$$\text{rate of disappearance of A} = \frac{-\Delta[A]}{\Delta t} = \frac{-d[A]}{dt}$$

$$\text{rate of appearance of C} = \frac{+\Delta[C]}{\Delta t} = \frac{+d[C]}{dt}$$

**THE COLLISION THEORY**

For most chemical reactions, the individual chemical steps that make up the mechanism of the reaction cannot be observed. The mechanism is really a theory about what occurs step-by-step as the reactants are converted to products. **The slowest step in a reaction mechanism determines the overall rate of reaction.**

Factors which affect the rate of reaction are explained by the collision theory. The collision theory simply states that for a reaction to occur, the species must collide with enough kinetic energy and in the correct orientation. By increasing the concentration of the reactants, you increase the number of collisions. You can increase the number of collisions by increasing the surface area of a solid reactant and increasing the temperature. Increasing the temperature of the reaction also increases the kinetic energy of the collision. The reactants must have the proper orientation for an effective collision. This is necessary to break existing bonds so new ones form.

Let's look at the reaction of hydrogen peroxide and iodide in aqueous solution to produce $I_3^-$. From our discussion above, the rate may be expressed as:

$$\text{rate} = -\frac{1}{3}\frac{d[I^-]}{dt} = -\frac{1}{2}\frac{d[H^+]}{dt} = \frac{-d[H_2O_2]}{dt}$$

The rate law for the appearance of products is:

$$\text{rate} = k[H_2O_2]^x\,[I^-]^y\,[H^+]^z$$

where x, y, and z are the reaction orders and k is the rate constant.

Expressing the rate by measuring the formation of products results in:

$$\text{rate} = \frac{d[I_3^-]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt}$$

Combining these two expressions gives us the general rate law for reaction (1):

$$\frac{d[I_3^-]}{dt} = k[H_2O_2]^x [H^+]^y [I^-]^z \qquad (2)$$

King[1] describes two possible reaction mechanisms. The first mechanism is dependent on $H^+$ and is described by

<u>Mechanism 1</u>:

$$H^+ + H_2O_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} HOOH_2^+ \qquad (3) \text{ fast}$$

$$HOOH_2^+ + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + HOI \qquad (4) \text{ slow}$$

$$HOI + H^+ \overset{k_2}{\rightarrow} H_2OI^+ \qquad (5) \text{ fast}$$

$$H_2OI^+ + I^- \overset{k_3}{\rightarrow} H_2O + I_2 \qquad (6) \text{ fast}$$

$$I_2 + I^- \overset{k_4}{\rightarrow} I_3^- \qquad (7) \text{ fast}$$

$$H_2O_2 + 2H^+ + 3I^- \rightarrow 2H_2O + I_3^-$$

Recall that the rate determining step is the slow step in the mechanism. The reacting species are obtained from the slowest step but the rate law may be expressed only in terms of the overall reactants. Based on this mechanistic path, what is the rate law for the reaction?

(1) King, E. L., <u>How Chemical Reactions Occur</u>, W. A. Benjamin Inc., pp 80-83, 1963.

Another possible mechanism for this reaction does not involve $H^+$. This mechanism can be described by:

**Mechanism 2:**

$H_2O_2 + I^- \longrightarrow OH^- + HOI$ (12) slow

$OH^- + H^+ \longrightarrow H_2O$ (13) fast

$HOI + H^+ \longrightarrow H_2^+OI$ (14) fast

$H_2^+OI + I^- \longrightarrow I_2 + H_2O$ (15) fast

$I_2 + I^- \longrightarrow I_3^-$ (16) fast

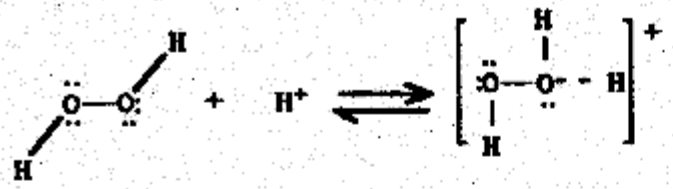
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$H_2O_2 + 2H^+ + 3I^- \longrightarrow 2H_2O + I_3^-$

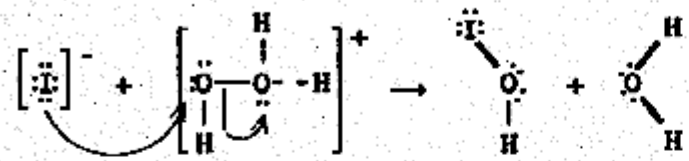
Based on this reaction path, what is the rate law expression for the reaction?

Notice that the first reaction mechanism results in a rate law that is dependent on $[H^+]$. A straightforward way to determine which mechanism is valid would be to do several reactions while changing the acidity of the solution. If no change in the rate occurs, we know that the rate is independent of $[H^+]$ ($y = 0$ for equation 2).

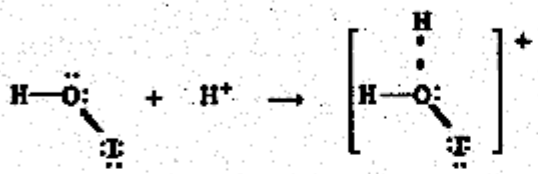
In order to visualize the reaction, you must think about the molecular interactions. For example, when the iodide ion reacts with the peroxide in acidic solution, equations 3 and 4, the sequence of reactions might appear as follows:



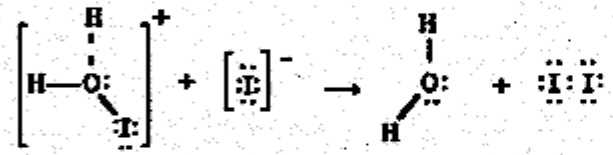
fast



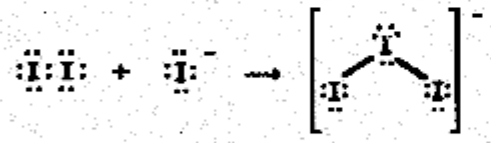
slow



fast



fast



fast

**What is the rate law for the reaction?**

Remember, the rate of a reaction is affected not only by the concentration of the reactants but also by the orientation of the molecules and their kinetic energy. The orientation and spatial relationship of the molecules are easier to visualize if you use VSEPR theory.

**PART I: TEMPERATURE EFFECTS**

1. For this experiment you will need aluminum foil and zinc. First, place four squares of zinc and four squares of aluminum on the reaction surface. Place five to ten drops of 0.01 M HCl on one square of zinc, five to ten drops of 0.1 M HCl on the second square, five to ten drops of 1.0 M HCl on the third, and five to ten drops of 6.0 M HCl on the last square of zinc. Repeat for the aluminum. Record your observations below. Include a description of the reaction and **times** from addition of reactants to <u>first</u> observable reaction:

| | Zinc | Aluminum |
|---|---|---|
| 6.0 M HCl | | |
| 1.0 M HCl | | |
| 0.1 M HCl | | |
| 0.01 M HCl | | |

2. Repeat the above experiment but add one drop of $Cu(NO_3)_2$ to the HCl (place the HCl on the metal first). Record your observations.

| | Zinc | Aluminum |
|---|---|---|
| $Cu(NO_3)_2$/ 6.0 M HCl | | |
| $Cu(NO_3)_2$/ 1.0 M HCl | | |
| $Cu(NO_3)_2$/ 0.1 M HCl | | |
| $Cu(NO_3)_2$/ 0.01 M HCl | | |

Does $Cu(NO_3)_2$ act as a catalyst? (Remember a catalyst must increase the rate of the <u>same</u> reaction)

3. Now place the metals on an ice cube and repeat the first series of experiments (without the $Cu(NO_3)_2$). Record your observations below.

| | Zinc | Aluminum |
|---|---|---|
| 6.0 M HCl | | |
| 1.0 M HCl | | |
| 0.1 M HCl | | |
| 0.01 M HCl | | |

**PART II: CONCENTRATION EFFECTS**

**A. Introductory Procedures**

1. You will use the digital volt-ohm meter (d-VOM) for this part of the experiment. If you have any questions regarding the use of the d-VOM, ask your instructor. The procedure to set up the d-VOM for use is:

a. Turn the main switch to ohms Ω.

b. Press the oval button until "kΩ" is displayed.

c. Plug the BLACK lead into the hole marked COM. Plug the RED lead into the hole marked V.

Connect the leads to the cadmium sulfide (CdS) photoelectric cell. The CdS Cell is encased in a plastic support, and the support inserted into one of the wells of a 96 cell tray. The top of the cell will be used as your reaction surface, and should be as level as possible.

2. The CdS cell responds to changes in light intensity with a change in resistance. **It is important that the amount of light reaching the cell remain constant throughout the experiment.**

a. Place your hand over the CdS cell. Did the resistance decrease or increase?

This is similar to what occurs as the $I_3^-$ concentration increases. The *change* in resistance is directly related to the change in concentration (rate of formation) of $I_3^-$. $I_3^-$ is a yellow species which absorbs light, reducing the amount of light reaching the CdS cell. **You must be very careful in controlling the drop size of your reactants.** While the rate law is dependent on the concentration of the reactants, the photoelectric cell is reacting to the amount of light which reaches the cell. The greater the

depth of the reaction solution, the lower the transmittance. This phenomenon is described by Beer's Law. This law states that the light transmitted through a solution decreases as the concentration of light absorbing material in the solution increases. We will express this as:

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

where A is the absorbance of the solution, $\epsilon$ is a constant known as the molar absorptivity, $\ell$ is the effective path length that the light travels through the solution, and [X] is the concentration of the light absorbing material. You can see how the drop size will effect $\ell$.

**B. Determination of Effect of Acid Concentration**

1. Place one drop of 1 M $H_2O_2$, two drops of buffer pH 1, and one drop 2 M NaI on top of the photoelectric cell. **Add the NaI last** and record the initital resistance reading. Continue to record the resistance every 15 seconds for 5 minutes.

2. Repeat this experiment but use the buffer pH 3 with the 1 M $H_2O_2$ and 2 M NaI. Record your results.

3. Again, repeat this experiment but use the buffer pH 6 with the 1 M $H_2O_2$ and 2 M NaI. Record your results.

## C. Initial Rate Determination

1. In class, we have discussed using the initial rate method to determine the rate law from experimentally measured data. Devise an experiment in which you can determine the rate law by varying the concentrations of NaI and $H_2O_2$. Use the buffer pH 6 for each experiment. The table below is probably a good starting point. You must determine the rate from the data you collect.

| Trial Run | Drops $H_2O_2$ | Initial $[H_2O_2]$ | Drops NaI | Initial [NaI] | Drops pH6 | Rate of Formation $I_3^-$ |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |

**CONCLUSIONS**

1. Graph time vs. resistance for the 1 M $H_2O_2$, 2 M NaI and buffer with pHs 1, 3, and 6. Place these graphs on the same graph paper. Use of a spreadsheet will be very helpful here.

a. What do these graphs tell you about the effect of acid concentration on the rate of reaction of iodide with hydrogen peroxide?

b. Write the rate law for this reaction based on whether path 1 or path 2 is supported by your data:

2. Graph time vs. resistance for the three experiments you conducted in the Initial Rate section of the lab. You may also place these graphs on the same sheet of graph paper.

3. What is the initial rate of each trial in question 2. You may determine this from your graphs by taking the slope of your curve at time = 0 (use only the first few data points). Recall that the rate of change of your measured resistance is equal to the rate of change in concentration of $I_3^-$.

4. Using the inital rate data, determine the order of each reactant in your rate law for the reaction of sodium iodide and hydrogen peroxide. Write the rate law:

5. Determine the rate constant for the rate law. Use the rate expression developed above.

**PRELAB PROBLEMS**

1. Using Lewis structures, draw a possible reaction for mechanism 2, eq. 12.

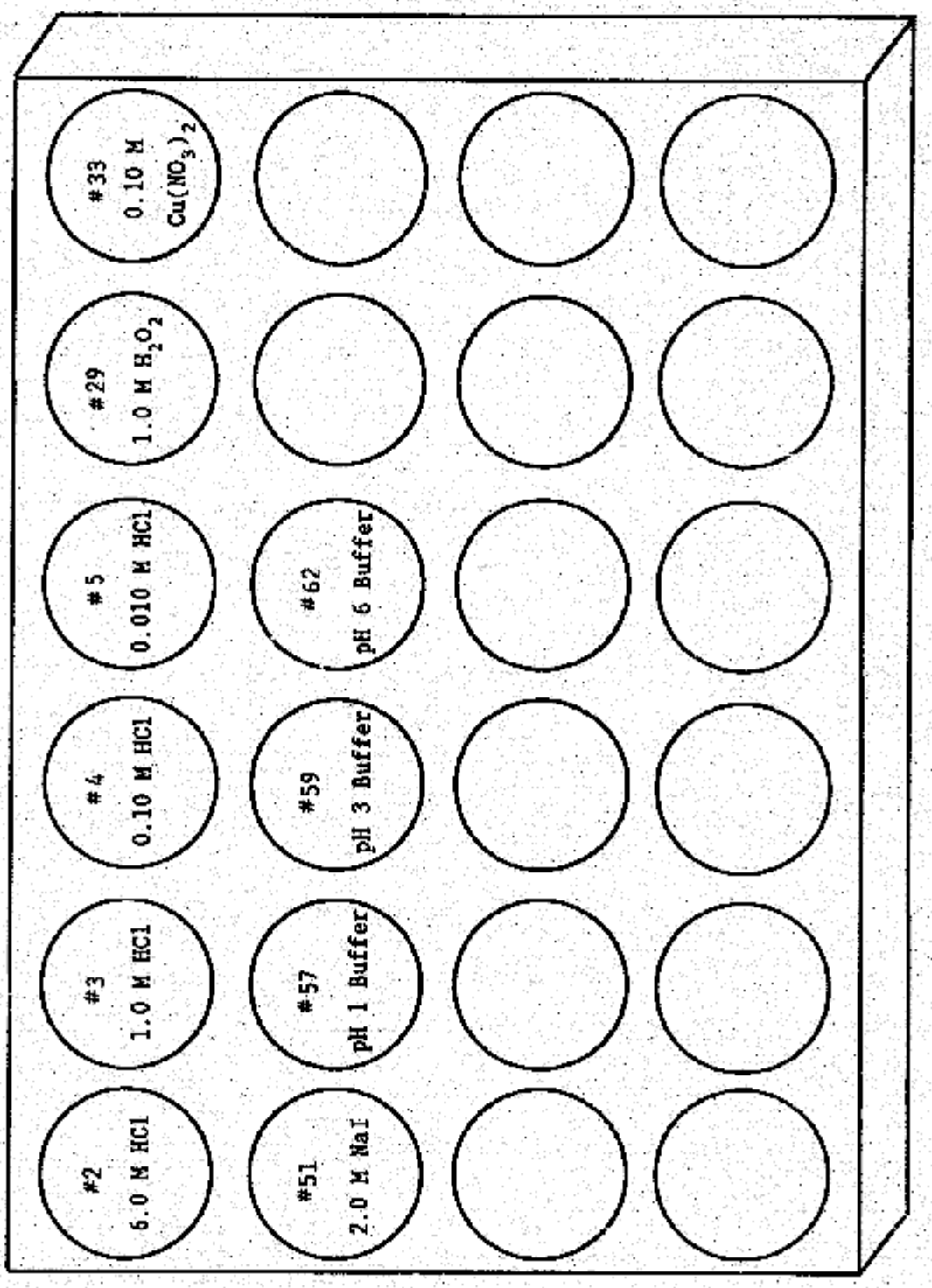
2. What color is the $I_3^-$ ion?

3. Write a balanced redox equation for the reaction of Al metal with HCl:

4. According to the Collision Theory, what two conditions must be met for a reaction to occur?

5. What is the general rate law for the following reaction?

$$H_2O_2 + 2H^+ + 3I^- \longrightarrow I_3^- + 2H_2O$$


#33
0.10 M
$Cu(NO_3)_2$
#29
1.0 M $H_2O_2$
#5
0.010 M HCl
#62
pH 6 Buffer
#4
0.10 M HCl
#59
pH 3 Buffer
#3
1.0 M HCl
#57
pH 1 Buffer
#2
6.0 M HCl
#51
2.0 M NaI

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# ELECTROCHEMISTRY
## Chemistry 131

## INTRODUCTION

Electrochemistry, which deals with the conversion between electrical energy and chemical energy, is an important area of chemistry that touches many aspects of our lives. Were it not for an application of electrochemistry in the form of batteries, we would still hand crank our cars to start them and wear windup watches. On the other hand, we would use slide rules rather than calculators. Other applications affecting our daily lives include electroplating and corrosion of metals. Electrochemical measurement techniques are used routinely to determine extremely low concentrations of ions in solutions, identify unknown compounds, monitor reaction rates, and study a whole host of other phenomena.

### Voltaic Cells

To convert the energy from a chemical reaction to electricity, a voltaic or galvanic cell (commonly known as a battery) is used. A voltaic cell operates on spontaneous oxidation-reduction reactions. The transfer of electrons between substances produces the electricity.

Voltaic cells are constructed to separate the oxidation half reaction from the reduction half-reaction. This separation forces electrons to flow through an external circuit where they can do work. We can construct a galvanic cell using the spontaneous reaction of copper metal and $Ag^+$ ions. In the reaction, electrons are transferred from the copper metal to the silver ions.

The balanced net ionic equation for this reaction is:

$$2Ag^+_{(aq)} + Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)} \qquad (1)$$

Which can be divided into oxidation and reduction half-reactions:

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^- \qquad (2)$$

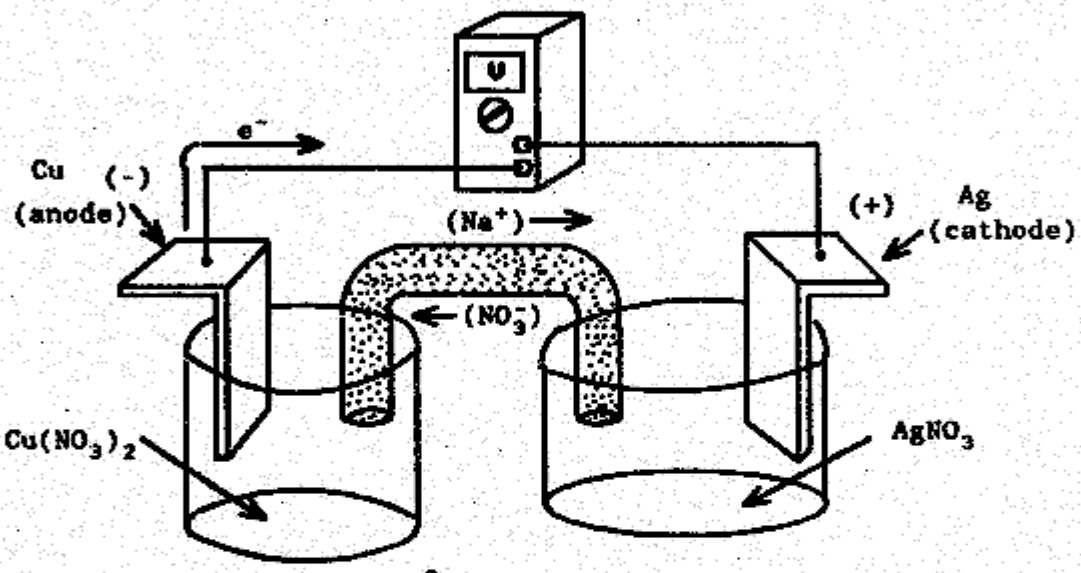
$$2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)} \qquad (3)$$

Equations 2 and 3 show what happened. The electrons lost from copper are used by $Ag^+$ ions to form silver metal while $Cu^{2+}$ goes into solution. Figure 1 shows a voltaic cell using these reactions.

We use a standard notation to describe galvanic cells. For the copper/silver cell, this notation is:

$$Cu(s) \,/\, Cu^{2+}(aq) \;\|\; Ag^+(aq) \,/\, Ag(s)$$

The slashed lines represent phase boundaries, the two solid lines represent half cell boundaries. By convention, the anode (oxidation reaction) is written first.




Voltaic Cell

Figure 1

According to equation 2, the Cu metal loses electrons (oxidation) forming $Cu^{2+}$ ions. These "lost" electrons travel through the wire to the Ag metal, and combine with the $Ag^+$ ions (reduction) in solution, and Ag is plated out on the Ag electrode. The *salt bridge* completes the circuit by allowing inert ions such as $Na^+$ and $NO_3^-$ to travel through the salt bridge and maintain ionic-neutrality of the solution. Without a salt bridge, no current can flow because as $Ag^+$ ions leave solution the remaining solution will have too many negatively charged nitrate ions, $NO_3^-$, left. By "intercepting" the flow of electrons outside of the cell, we can use them to drive a motor and produce work or light a lamp or power a calculator. This will cause a positive deflection on a voltmeter, verifying current flow as shown above. *Oxidation* occurs at the *anode, reduction* at the *cathode*. An easy way to remember this: both oxidation and anode begin with vowels while reduction and cathode begin with consonants.

**Electrolytic Cells**

An electrolytic cell is similar to a galvanic cell, but instead of obtaining electrical energy from spontaneous reactions, an electric source is attached to the electrodes "forcing" electrons to move in the opposite direction. Thus a non-spontaneous reaction can be forced to occur by supplying electrical current. Some uses of electrolytic cells include electroplating metals onto other metals, refining or purifying metals, charging "rechargeable" batteries (car batteries, nickel/cadmium batteries, etc.), decomposing water, and obtaining pure metals from their ores.

This last application is extremely important in the production of aluminum from its ore, $Al_2O_3$. Hall discovered this electrolytic process while still a college student in 1886. Before his discovery, aluminum was so expensive that the rich would flaunt their wealth by throwing dinner parties using aluminum utensils. Today, production of one mole of aluminum from its ore requires 30,000 joules of energy. Recycling aluminum requires only 26.1 joules per mole (the amount of energy required to melt aluminum). Thus, the emphasis on recycling aluminum rather than producing it from its ore is quite obvious.

**Standard Potentials and E° Calculations**

By using half-cell potentials, you can determine the voltage (potential) that any two half-reactions will produce. The potentials are not an absolute figure, but are measured relative to a reference half-reaction. The standard reduction potentials we see in tables in our book and on the classroom wall are measured against the Normal Hydrogen Electrode (NHE) which has a reduction half-reaction:

$$2H^+_{(aq)} + 2e^- \text{ -------> } H_{2(g)} \qquad (4)$$

The NHE has been assigned an E° or voltage of 0.00 V. Actually any reaction could be used as the reference but since hydrogen has been chosen, we still continue with it. The symbol E° means standard half-reaction or "half-cell" potential in which the reactant and product solutions are 1.00 M (1 atm for gases) and the metals are pure crystals. For convenience, we normally tabulate the E° values at 25°C, but it's not necessary. This method enables us to determine the potential for numerous half-reactions. By listing all half-reactions as reduction half-reactions, we generate a table of standard reduction potentials.

A table of standard reduction potentials enables us to determine the potential of a redox reaction, determine the order of reactivity of some species towards others, and to determine which of two species is more susceptible towards reduction or oxidation in a

spontaneous redox reaction. A positive E° value indicates that the substance will spontaneously reduce relative to equation 4, while negative values mean a spontaneous oxidation will occur relative to equation 4. By simply adding the $E_{ox}$ and $E_{red}$ values, you can obtain E°. The E° value for reaction 1 is simply the sum of the E° values for reactions 2 and 3. Remember $E°_{ox} = -E°_{red}$ for a particular half-reaction.

$$E° = E°_{oxidation} + E°_{reduction} = -0.337\ V + 0.7994\ V = .462V \quad (5)$$

Note that the $E_{ox}$ and $E_{red}$ values are **not** multiplied by the stoichiometrix coefficients used to balance the redox equation.

**Nernst Equation**

In the late 1800's, a German chemist named Walter Nernst was studying the thermodynamics of electrolytic solutions. Through his research he developed a formula to calculate the potential of a cell that was not at standard temperature, pressure and concentration. It is called the Nernst equation. Using equations we covered in this and earlier chapters, we can arrive at this equation. Gibbs standard free energies ($\Delta G$) are given by equations 6 and 7.

$$\Delta G° = -nFE° \quad (6)$$

$$\Delta G = -nFE \quad (7)$$

Here n equals the moles of electrons ($e^-$) transferred in the reaction and F is Faraday's Constant (96,485 Coulombs/mole $e^-$). Gibbs free energy is also given by equation 8.

$$\Delta G = \Delta G° + RT \ln Q \quad (8)$$

where R is the gas constant (8.314 J $K^{-1}mole^{-1}$), T the temperature in Kelvin, and Q the reaction quotient ([Products]/[Reactants]). Substituting equations 6 and 7 into equation 8 we obtain equation 9.

$$-nFE = -nFE° + RT \ln Q \quad (9)$$

Dividing both sides by -nF we obtain equation 10, which is the Nernst equation.

$$E = E° + (RT/-nF) \ln Q \quad (10)$$

Since we usually conduct redox reactions at room temperature (298K), the quantity (RT/nF) conveniently becomes 0.0257/n and the Nernst equation at these conditions becomes

$$E = E° - (0.0257/n) \ln Q \quad (11)$$

**Corrosion/Corrosion Protection**

Corrosion is metal deterioration. It's mainly an electrochemical process, and under the right conditions, it occurs spontaneously in nature. The cost to the U.S. economy in 1984 due to metallic corrosion alone was over $80 billion.[1] Thus, corrosion is a significant problem. With so many aircraft constantly exposed to the elements, corrosion is also a major Air Force concern.

Before we can examine ways to protect against corrosion, we must first understand what happens during corrosion. Corrosion results from the operation of spontaneous electrochemical cells on the surface of the metal being considered. We'll limit our discussion here to steel (iron) samples. You might wish to imagine the body of a new automobile or a Soviet Mig 25 during the following discussion.

As in all electrochemical reactions, oxidation happens at the anode. This occurs because the anode is more easily oxidized than the other metal in the cell. For solid metal, oxidation forms metal cations which are soluble in water. So how does a steel car body rust if it consists only of steel?

Well, in order for corrosion to occur, water must be present. Dissolved in the water is oxygen, which undergoes the following reduction half-reaction:

$$O_2 + 2H_2O + 4e^- \text{------>} 4OH^-$$

The other half-reaction is the oxidation of iron:

$$Fe_{(s)} \text{------>} Fe^{2+}_{(aq)} + 2e^-$$

Write the overall oxidation/reduction reaction that occurs during the formation of rust:

Thus cars "rust-out" because of the air. Of course the process happens rapidly if certain other conditions are present. You must have some contact between the solutions of reactants. Water works best for this. The water works better if some ions present are already in solution (what does this provide?). Some states sprinkle rock salt on snowy roads. This provides all of the requirements. A small scratch in the paint, moisture, and an ionic solution, and the result is rust on your new car.

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1. Chang, R., *Chemistry*, 3rd ed., Random House, Inc., New York, 1988, pp. 784-785.

As you recall, E° values apply only to pure crystalline metal samples. Most steel samples do not have a uniform crystalline structure; instead, they have many small areas of differing crystal structure due to stresses that occur during processing of the metals. These different regions have different E° values and this results in the formation of a voltaic cell. Thus, in steel samples, some of these regions serve as cathodes while others serve as anodes. This explains why rust occurs at separate, distinct points all over the metal surface instead of covering the entire metal surface uniformly.

One obvious solution to this problem is to produce steel with one uniform crystalline structure. Technologically, this would be extremely expensive, if not impossible at this time. Therefore, some other means of protecting steel (iron) structures must be devised. Some of the simpler and less effective of these means include surface coverings (paint, etc.) and passivation. Passivation is the process of coating the surface of the steel sample with another metal (usually less reactive or not as easily oxidized as steel.) Both of these methods protect the steel by covering it. Unfortunately, once the surface coating is removed or scratched off, rust develops.

A better way to protect the steel would be to electrically connect the steel to be protected to a more active (more easily oxidizable) metal, such as magnesium. In this way, the steel becomes the cathode and the magnesium becomes the "sacrificial" anode. This process is known as cathodic protection. In order to incorporate cathodic protection, the sacrificial metal must have a lower reduction potential than the metal to be protected.

**EXPERIMENTAL**

**A. Voltaic Cells (Batteries):**

In this experiment, you will set up voltaic cells, as in Figure 1, but on a micro-scale. Refer to Figure 1 often to identify the parts of the cell with your setup.

1. Cut a piece of rectangular filter paper in half so you have two squares. Fold it in fourths and cut it to form a "+", as demonstrated by your instructor. Save the leftover pieces for Parts C and D.

2. Take some of the copper, zinc, lead, and iron and lightly sand off the oxide layer on them.

**NOTE:** Read Steps 3-5 before performing them, because you'll want to take quick measurements for more accurate results.

3. Place the four metals at different corners of your newly cut filter paper. Place 5-10 drops of 0.10 M $NaNO_3$ solution in the middle of the filter paper. What function does the $NaNO_3$ perform?

4. Place a few drops of 0.10 M $Cu(NO_3)_2$ to the side of or underneath the copper. Do the same with the 0.10 M $FeSO_4$, 0.10 M $Pb(NO_3)_2$, and 0.10 M $Zn(NO_3)_2$ solutions and their respective metals. The drops of solution must touch their metals and these solutions must just touch the $NaNO_3$ solution.

5. Take your multimeter and select DC volts (VDC) and measure the voltage between the following:

a. Make sure your leads touch bare metal and are not themselves immersed into the solution.

b. Switch leads from your multimeter on the metals if you get a negative voltage (you want a positive voltage indicating a spontaneous reaction).

| | E(V) | | E(V) |
|---|---|---|---|
| Cu and Zn | _____ | Cu and Fe | _____ |
| Cu and Pb | _____ | | |

6. Why are these values recorded as E and not E°?

7. Calculate the theoretical E° values for the three voltaic cells you constructed (using a Table of Standard Reduction Potentials) and write the two half-reactions for each cell as they occurred.

a. Cu and Zn E°(V)

Reduction Half-reaction:

Oxidation Half-reaction:

Measured E = _____ Theoretical E° = _____

b. Cu and Pb E°(V)

Reduction Half-reaction:

Oxidation Half-reaction:

Measured E = _____ Theoretical E° = _____

c. Cu and Fe E°(V)

Reduction Half-reaction:

Oxidation Half-reaction:

Measured E = _____ Theoretical E° = _____

8. Why does the measured E not equal the theoretical E°?

## B. Reduction Potentials:

As you recall, the standard reduction potentials of all elements are measured relative to the reduction of the following reaction:

$$2H^+_{(aq)} + 2e^- \text{ ------> } H_{2(g)} \quad E° = 0.00 \text{ Volts} \qquad (12)$$

In this part of the lab you will construct a table of reduction potentials for some metals, but you will use the following as the reference:

$$Pb^{2+}_{(aq)} + 2e^- \text{ -----> } Pb_{(s)} \quad E° = 0.00 \text{ Volts} \qquad (13)$$

**Note:** Redox processes could be measured against any reference as long as they're all measured against that same reference.

1. Using the same setup as before, measure the potential of the following metals and their 0.10 M solutions against the $Pb/Pb^{2+}$ system:

Al, Cu, Fe, Pb, Mg, Zn.

a. Based on your knowledge of the table of **standard reduction potentials**, predict the order of reduction potentials vs. Pb before you measure them.

b. Make sure you first sand any oxide layers off the metals. To look at the reduction half-reactions for the metals, put the negative (black) lead on the $Pb/Pb^{2+}$ electrode. The negative lead is the source of electrons; therefore with the black lead on Pb, you know Pb is being oxidized.

c. In making *your table*, report all values (even the negative ones), rank order all potentials, and write half-reactions as reduction reactions.

| Metal | Reduction Potential vs. $Pb/Pb^{2+}$ |
|---|---|
| Al | |
| Cu | |
| Fe | |
| Pb | |
| Mg | |
| Zn | |

**Using this information, write your Table of Standard Reduction Potentials below. THIS IS DATA FROM YOUR EXPERIMENTS. DO NOT USE A TABLE OF STANDARD REDUCTION POTENTIALS FOR THIS TABLE.**

**TABLE OF STANDARD REDUCTION POTENTIALS**

| Reduction Half-Reaction | $E^\circ$ (volts) |
|---|---|

**C. Nernst Equation:**

1. Using the same procedure as in Part A, set up the following copper and lead voltaic cell:

$Pb_{(s)}/\ Pb^{2+}(aq,\ 0.10\ M)\ ||\ Cu^{2+}(aq,\ 0.10M)/\ Cu_{(s)}$

2. Measure E for this cell.

E = _____

b. Calculate E° for this cell using a table of Standard Reduction Potentials.

c. Using the Nernst equation, calculate E for the 0.10 M cell.

d. Does the calculated E for the 0.1 M cell equal the E° for the standard 1.0 M cell? *Why?*

2. Now measure E as the concentrations of $Pb^{2+}$ and $Cu^{2+}$ are changed. Fill out the table and show your calculations for the E values. Use leftover filter paper pieces from Part A.

| $[Cu^{2+}]$ | $[Pb^{2+}]$ | $E_{meas}$(V) | $E_{calc}$(V) |
|---|---|---|---|
| 1.00 M | 0.10 M | _____ | _____ |
| 1.00 M | 0.0010 M | _____ | _____ |

Calculations for E when $[Cu^{2+}]$ = 1.00 M and $[Pb^{2+}]$ = 0.10 M:

Calculations for E when $[Cu^{2+}] = 1.00$ M and $[Pb^{2+}] = 0.0010$ M:

3. It is possible to set up a voltaic cell that is driven by a concentration difference. A potential will continue to exist between the two half cells until their concentrations are equal. Investigate this by setting up the following cell:

$$Cu_{(s)} / Cu^{2+}(aq,\ 0.10M) \parallel Cu^{2+}(aq,\ 1.00\ M) / Cu_{(s)}$$

a. Measure E for this cell. (Remember to switch the meter leads if needed to obtain a positive voltage.)

E = _____

b. Under standard conditions, what would E° for this cell be?

c. Deviations from standard conditions (one molar concentration for ions, one atmosphere pressure, and standard phases at 25° C) cause the deviation of your observed E in paragraph C.3.a. from E°. Use the Nernst Equation to calculate E for this cell. Compare your measured and calculated values for E.

d. Are there other conditions besides standard conditions that will give an E=0 for this cell? What are they?

**D. Electrolytic Cells:**

**1. Electrolysis of Copper:**

**a. Partially fill one well in your reaction tray with 1.00 M $Cu(NO_3)_2$. Clean the oxide layer off a nail with 1 M HCl and place it into the solution. Wait for about 30 seconds. What occurred?**

**b. Write the balanced redox equation for the reaction you just observed:**

**c. Remove the nail from solution and describe it.**

**d. What is the coating on the nail?**

**e. What half-reactions took place to produce this coating?**

**Oxidation half-reaction:**

**Reduction half-reaction:**

**f. Since we didn't add any energy to make this reaction occur, it's a *spontaneous process*. As in Part A, we could have separated the two half-reactions of the above redox reaction and produced a galvanic cell; however, we'll now make an electrolytic cell and reverse this spontaneous process. To do this, hook up the 9-volt battery to the nail and to a graphite electrode, then immerse both in the 1.00 M $Cu(NO_3)_2$ solution. Will you need to hook up the positive or negative lead to the nail? Why? (Hint, the positive lead withdraws electrons into the battery while the negative lead "pumps" electrons from the battery.) Stop the experiment shortly after the nail begins to bubble violently. <u>Before</u> stopping the experiment, observe the nail in the solution. Does anything happen when you withdraw it from the solution? 10-15 seconds after that?**

**g. To show that the $Cu(NO_3)_2$ solution will not react spontaneously with the graphite, place a piece of graphite in the solution for about one minute. Withdraw the graphite and describe significant changes, if any.**

h. Did your electrolytic cell cause the spontaneous reaction above (steps 2-6) to be reversed? Explain how you know this.

i. Why did the nail regain the copper color about 5-10 seconds after withdrawing it from solution?

j. Write the half-reaction which occurred on the graphite.

k. Did your nail perform as an anode or cathode? Explain your answer.

l. Write the half-reaction which occurred on the nail once the plated metal was removed.

2. Electrolysis of Water

Hydrogen is an excellent fuel that someday may be used in place of jet fuel for aircraft or gasoline for cars. Now it is used in the space program to propel the Space Shuttle into orbit. Hydrogen though, does not exist by itself in abundant quantities on earth (most of it has escaped the earth's gravitational pull over the ages). One method of producing it is through the electrolysis of water, that is, using electricity to break water into $H_2$ and $O_2$.

a. Make an electrolytic cell using your 9-volt battery and graphite electrodes to electrolyze water. Use 0.10 M $NaNO_3$ solution and add 4-6 drops of Yamada indicator. Why must you use water with .10 M $NaNO_3$ in it?

b. Connect the battery and list your observations.

c. What is the color around the cathode? What gas is evolving from the cathode? (Hint: To determine which electrode is the cathode, look at the oxidation and reduction half-reactions for the electrolysis of water in your text. Use the color of Yamada indicator to determine which half-reaction is being produced at each electrode. Remember that Yamada gives *red in acid* and *blue in base*.)

d. Write the half-reaction occurring at the cathode.

e. What color exists at the anode and what gas evolves there? Write the half-reaction occurring at the anode.

**E. Cathodic Protection:**

1. Which of the metals you have been given could be used to cathodically protect an iron nail? (Which metals oxidize easier than iron?)

2. Of these metals, which do you think would *best* protect iron from corrosion?

3. Wrap a piece of the metal you identified in paragraph E.2. around the head of a nail. Place an "unprotected" nail and the "protected" nail in plastic cups containing enough de-ionized $H_2O$ to cover the nails completely and add-4-6 drops of Yamada indicator. What happens? (The reaction may take up to 10 minutes to occur.)

4. Repeat this for another one of the metals identified in paragraph E.1. Observations?

**F. Application Experiments:**

1. Recovering Iodine From Solution

Given an aqueous solution of NaI, we can set up an electrolytic cell to collect $I_2$.

a. When NaI is placed into water it dissociates into what ions?

b. We want to convert the iodide ion, $I^-$, to $I_2$. Write the half-reaction for this process. Is this an oxidation or reduction reaction?

c. In order to make the electrolytic cell, you'll use two graphite electrodes connected to the battery. Use the graphite electrodes from the electrolysis experiment. Do not use the Yamada indicator in this experiment. (Graphite is a common "inert" electrode. It plays no part in the balanced redox equation; it simply acts as a reaction surface, allowing the electrons to flow in the cell.)

d. Which electrode on the battery (positive or negative) will cause the half-reaction in paragraph F.1.b.?

e. Will it be the anode or cathode? Why?

f. Perform the experiment using 0.10 M NaI. Report your procedure, observations and results.

The black color emanating from one of the electrodes is the $I_2$. The yellow color is $I_3^-$ (which you saw in previous experiments.)

2. Optional Experiments. Additional experimentation is allowed <u>if</u> cleared by your instructor. Use the next page to design your experiment <u>before</u> you ask your instructor's permission. Your experimental design must include a background statement (what chemical theory do you plan to use), experimental section detailing what you will do, and a conclusion section. Some ideas to help you get started:

a. Electroplate an object. What voltage is produced during your experiment?

b. Voltaic cells in series vs. single cells.

c. Voltaic cells connected in parallel vs. single cells or series cells.

## OPTIONAL EXPERIMENT DESIGN PAGE

**DISCUSSION:**

1. If we were to construct a battery in which the oxidation of Pb would be one half-reaction, which metal in **YOUR TABLE** of half-reactions would give us the highest voltage? Justify your answer.

2. Using your data collected for the Cu and Pb galvanic cell, draw a schematic of this cell. Label all important parts, give the oxidation and reduction half-reactions for the appropriate electrodes and show the correct flow of electrons and ions. Draw the line notation for the cell. Refer to Figure 1 and/or your text for help. (You can draw it like Figure 1 or draw a side view of your experiment.)

3. Define standard state for a solid, liquid, gas, and ion in solution. Are we justified in comparing the experimental results to the theoretical values for $E^\circ$? Explain your answer.

4. Based on **YOUR TABLE** of Standard Reduction Potentials:

   a. Which metal has the greatest potential to be oxidized?

   b. Which metal has the lowest potential to be oxidized?

   c. Give an example where these metals are used by society. Do the applications fit the behavior of the metal toward oxidation? (See Chapter 22 in the text for a discussion on the uses of these metals.)

5. Acids can oxidize some metals. Based on oxidation potentials, would HCl oxidize Mg and Zn? Justify your answer using half reactions.

6. For the voltaic cell in Figure 1, would you expect the mass of the Cu electrode to increase or decrease? Would the mass of the Ag electrode increase or decrease? Explain.

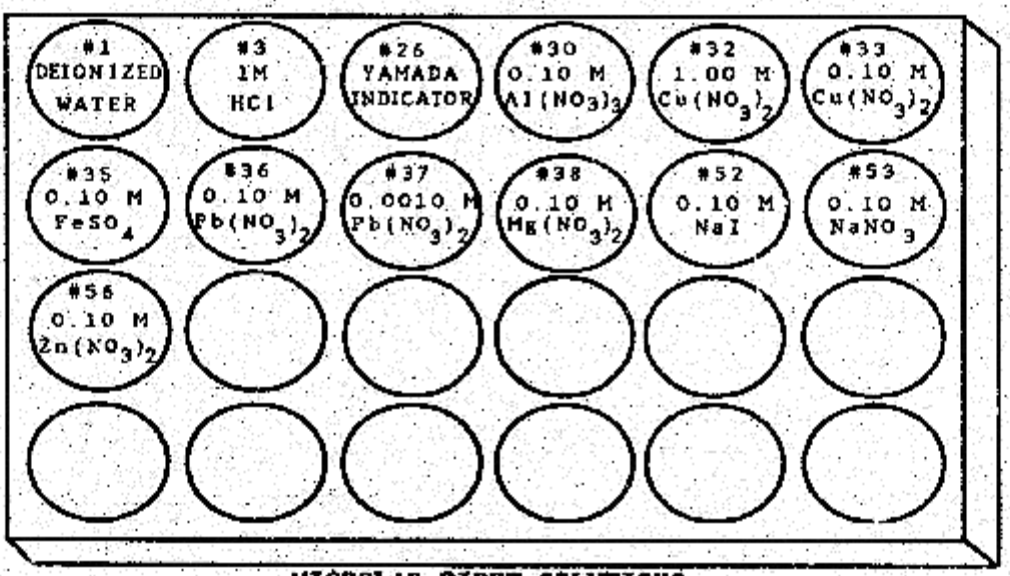
7. Briefly describe the differences between a voltaic cell and an electrolytic cell.

8. Why were there differences between your measured E and the calculated E° in Part C?

9. If we bubbled $Cl_2$ gas through our 0.10 M NaI solution, could we obtain $I_2$? Explain using concepts you have learned in electrochemistry.

10. Explain how the Nernst Equation can be used to determine the equilibrium constant for a balanced redox reaction.

11. Should a change in temperature affect E° for a cell? Why?




**MICROLAB PIPET SOLUTIONS**

**ELECTROCHEMISTRY LABORATORY**

**ELECTROCHEMISTRY SMALL-SCALE LAB**
**PRELAB QUESTIONS**

These questions must be completed BEFORE coming to lab. If you cannot answer all of them, reread this handout, and try them again.

1. a. What is oxidation?

   b. Reduction?

2. a. Draw a Voltaic Cell based on the following:

   $Zn_{(s)}$ / $Zn(NO_3)_{2(aq)}$ || $Cu(NO_3)_{2(aq)}$ / $Cu_{(s)}$

   b. Label the anode, cathode, salt bridge and indicate the flow of electrons and ions.

   c. Write the oxidation and reduction reactions.

   d. Write the overall net reaction.

3. Calculate the voltage you could get out of a voltaic cell made of silver with its ion, $Ag^+$, and tin with its ion, $Sn^{2+}$. (Hint: You do not need to balance the redox reaction. Use the Standard Reduction Potentials Table on page 740 of your text.

   a. Write the reduction half-reactions.

| | Reduction Half-reaction | E° (V) |
|---|---|---|
| Silver: | _____ | _____ |
| Tin: | _____ | _____ |

b. Write the oxidation and reduction reactions that occur in this cell.

Oxidation reaction: _____

Reduction reaction: _____

c. Write the overall net reaction.

d. Calculate E°.

Your E° should be positive since this is a spontaneous electrochemical cell. If it is not, you need to switch the direction of your oxidation and reduction reactions.

# ORGANIC LABORATORY
## Chemistry 131

**INTRODUCTION**

Organic chemistry is the chemistry of carbon compounds. Prior to 1828, the term "organic" was used to describe chemicals that had come from animals or plants. In that year, Friedrich Wohler showed that organic chemicals could be synthesized from inorganic sources. He synthesized urea simply by heating the salt ammonium cyanate.

$$NH_4OCN \xrightarrow{\Delta} H_2N\cdot\overset{O}{\overset{\|}{C}}-NH_2$$

(inorganic) (organic)

Organic chemistry is a very large field of chemistry. Over 7 million organic chemicals are known. Our lives are surrounded by, and sustained by organic chemistry. For this reason it is also referred to as the chemistry of life. The large number of organic compounds can be understood more easily by subdividing them into groups. These groups can arise from the classification of organic compounds based on their physical characteristics and reactions. These two factors are influenced by the "functional groups" within each molecule.

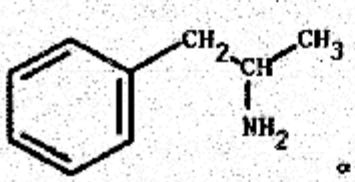
**Theory**

A functional group is a group of atoms that act as a site where chemical reactions may occur. Reactions may also occur in the proximity of functional groups. In this lab, you will investigate several important functional groups. These include amines, carboxylic acids, alcohols, aldehydes, ketones, and esters. Examples of each are shown in Figure 1. These eight functional groups are found in the majority of organic compounds in your body and in nature.

| | | |
|---|---|---|
| $R-\overset{H}{\overset{\|}{N}}-H$ | $R-\overset{O}{\overset{\|\|}{C}}-H$ | $R-\overset{O}{\overset{\|\|}{C}}-R'$ |
| **AMINE** | **ALDEHYDE** | **KETONE** |
| $R-\overset{R''}{\overset{\|}{C}}-OH$ | $R-\overset{O}{\overset{\|\|}{C}}-OH$ | $R-\overset{O}{\overset{\|\|}{C}}-OR'$ |
| **ALCOHOL** | **CARBOXYLIC ACID** | **ESTER** |
| $R-\overset{H}{\overset{\|}{N}}-\overset{O}{\overset{\|\|}{C}}-R'$ | $R-\overset{O}{\overset{\|\|}{C}}-X$ | |
| **AMIDE** | **ACID HALIDE** | |

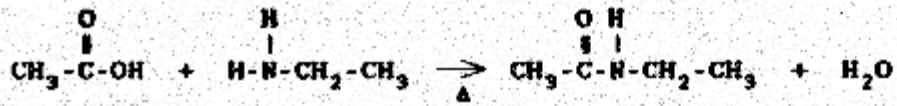
**FIGURE 1**
**Organic Functional Groups**

**Amines** are characterized as bases, and generally are polar. This polarity is due to a lone pair of electrons on the nitrogen and differences in the electronegativities of other substituents on the nitrogen. All amino acids contain an amine group (as well as a carboxylic acid group). Many pharmaceuticals also contain amines. An example is amphetamine (e.g., α-methylbenzeneethanamine), which stimulates the central nervous system and is addictive.



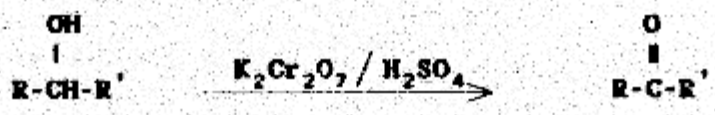
α - Methylbenzeneethanamine

An important reaction of amines is the condensation reaction with carboxylic acids to form an amide. This reaction can be used to produce polymeric chains such as nylon:



acetic acid ethyl amine ethyl acetamide

**Alcohols** are common organic substances that are encountered everyday. Ethyl alcohol (grain alcohol) is found in beverages, over the counter drugs, and cosmetics. Methyl alcohol (wood alcohol) is used as a fuel. Secondary alcohols react to form ketones in the presence of oxidizing agents. Potassium dichromate may be used as the oxidizing agent and the reaction is accompanied by a color change because dichromate is reduced to $Cr^{3+}$. The general reaction is:



This reaction will be done as a demonstration during this lab using isopropyl alcohol (rubbing alcohol) and acetone (the dimethyl ketone used in fingernail polish remover). You should note this is an oxidation-reduction reaction. What is being reduced? Write the reduction half-reaction in the box below:

**Aldehydes** are good solvents for polar substances such as alcohols. Formaldehyde is a gas that is used in aqueous solutions called formalin. Formaldehyde is used to preserve biological

specimens and as the basis of many glues, resins, and polymers. Acetaldehyde is used in its trimeric form as a sedative. Aldehydes react to form carboxylic acids in the presence of oxidizing agents. A qualitative test for aldehydes is the Tollens test. Tollens Reagent contains the silver ammonium ion, $Ag(NH_3)_2^+$, and will distinguish an aldehyde from a ketone, even though their functional groups are similiar. As the aldehyde is oxidized, the silver is reduced to a solid. A silver mirror will then form on the surface of the test tube (if the glass is clean). A finely divided black precipitate of silver appears if the glass isn't clean. The general reaction is:

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + 2\ Ag(NH_3)_2^+ + 3\ OH^- \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^- + 2\ Ag_{(s)} + 4\ NH_3 + 2\ H_2O$$

**Carboxylic acids** have characteristically sour tastes and odors. Acetic acid is an example of a carboxylic acid, and is primarily responsible for the smell of vinegar. Carboxylic acids are easily converted to esters (R-CO-O-R') which have characteristically pleasing odors.

Several functional groups are classified as derivatives of carboxylic acids. These include esters, amides, acid chlorides, and acid anhydrides.

**Esters** are quite common in nature and are easily identified by their unique odors. Isoamyl acetate has a banana smell, while methyl butyrate smells like apples. Ethyl butyrate is very structurally similar to methyl butyrate, but smells like pineapples instead of apples. Three other esters with distinct odors are isobutyl propionate, n-propyl acetate, and octyl acetate which smell like rum, pears, and oranges respectively.

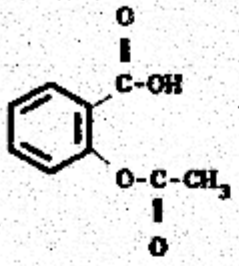
Aspirin (acetylsalicylic acid), an ester, is perhaps the most widely used drug in the world. Since 1899, when aspirin was introduced as a mild analgesic and antipyretic, it has become the layman's first line of defense against most minor discomforts such as colds and headaches. It has four helpful effects:

1. Analgesic. It relieves pain rapidly, inexpensively, and effectively.

2. Antipyretic. This means it brings down fever by increasing sweating and the flow of blood near the skin's surface.

3. Antirheumatic. It reduces the inflammation of and pain in the joints, permitting mobility.

4. Uricosuric. It decreases the deposits of urate that form in the joints.

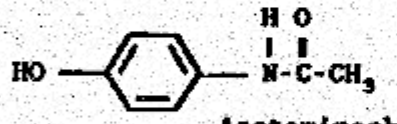


Aspirin

The reaction between carboxylic acidr and alcohols is a simple way to prepare esters. An example reaction is shown below. Water is lost to yield the ester.

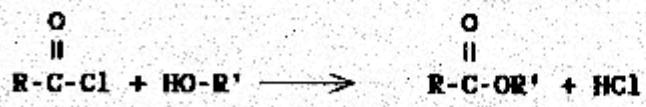


**Amides:** Acetaminophen is an amide more commonly known by the trade names Tylenol® and Datril®. It has important pain relief and fever reduction properties, but does not relieve inflammation as does aspirin. Its structure is:

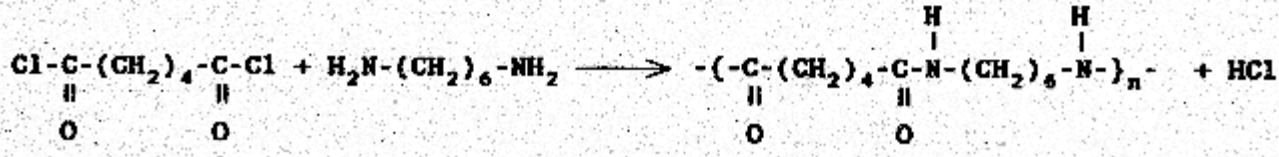


Acetominophen

One of the many uses of **acid chlorides** (and in general any acid halide) is in condensation reactions with amines to form polymers. During the polymer demonstration your instructor will make nylon using an acid chloride (adipoyl chloride) and an amine (hexamethylene diamine). The condensation reaction has the general form:



The condensation polymerization of nylon is:

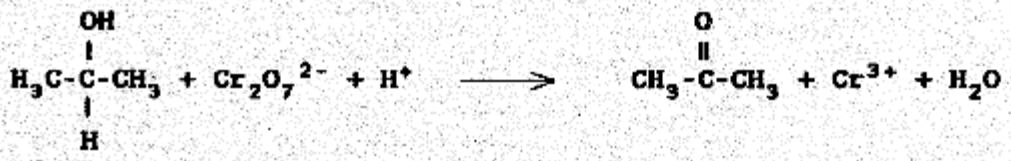


adipoyl chloride — hexamethylene diamine — nylon 6-6 polyamide

**EXPERIMENTAL**

**A. Demonstration: Ketone Preparation From an Alcohol**

1. Your instructor will demonstrate the oxidation of isopropyl alcohol to acetone using potassium dichromate in sulfuric acid. The unbalanced reaction is:



2. What color change did you see? What change in oxidation number is this color change due to?

3. Write the balanced equation using the redox half-reaction method. You will need to know that the central carbon atom in isopropyl alcohol has an oxidation state of 0 (zero), while the same carbon in acetone has an oxidation state of +2.

**B. Procedures**

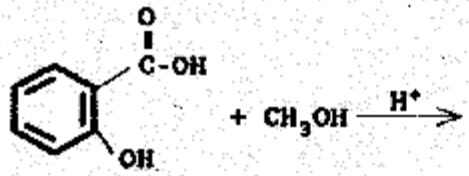
1. Synthesis of Methyl Salicylate: Condensation of a carboxylic acid with an alcohol.

a. Place a small amount (about the size of an aspirin tablet) of salicylic acid in a large test tube. Add 5 mL of methanol (CAUTION: methanol is flammable) and two drops of concentrated sulfuric acid.

b. Heat in a water bath set up by your instructor for three to five minutes. For safety considerations, no flame should be used to warm the reactants.

c. Carefully smell the product. If needed, the odor may be made more apparent by pouring the product onto 25 mL of ice. Describe the smell.

d. Complete the following reaction of methanol and salicylic acid:



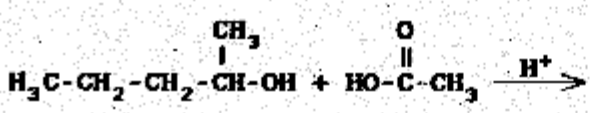
2. Synthesis of Isoamyl Acetate:

a. Place three drops of isoamyl alcohol (CAUTION: flammable), two drops of glacial acetic acid, and one drop of 3.0 M sulfuric acid into a test tube. (CAUTION: These are concentrated acids, avoid skin contact)

b. Carefully heat the test tube in a hot water bath for three to five minutes. (CAUTION: Keep the flammable solution away from flame. Hot sulfuric acid is extremely corrosive.)

c. Carefully smell the product. Record the smell below:

d. Complete the following reaction for the synthesis you have just done:



3. Synthesis of n-Propyl Acetate:

a. Add one mL of n-propanol ($CH_3CH_2CH_2OH$) to one mL acetic acid in a test tube. Add three drops of 3.0 M sulfuric acid to this mixture.

b. Heat the solution in boiling water for three to five minutes. (CAUTION: Keep the flammable solution away from the flame. Hot sulfuric acid is extremely corrosive.)

c. Carefully sniff the products. Record the smell below:

d. Write the condensation reaction between acetic acid and n-propanol in the box below:

4. Tollens Test: Detection of Aldehydes

a. Add one mL of 5% silver nitrate solution (CAUTION: Do not get silver nitrate on your skin) to a clean test tube. Add one drop of 1.0 M sodium hydroxide to the silver nitrate. A brown precipitate of silver oxide should form.

b. Write the reaction for the formation of this brown precipitate:

c. Now add three drops of 6.0 M ammonium hydroxide to the tube. Swirl the test tube (careful not to spill any solution) until all of the precipitate is dissolved. This is the Tollens Reagent.

d. Perform the Tollens test for an aldehyde by adding one drop of formalin to the Tollens Reagent. Describe what happened:

e. When Tollens Reagent reacts with formalin, an oxidation-reduction occurs.

What is the reduction half-reaction?

What is the oxidation half-reaction?

5. Sniff Tests of Other Organic Compounds:

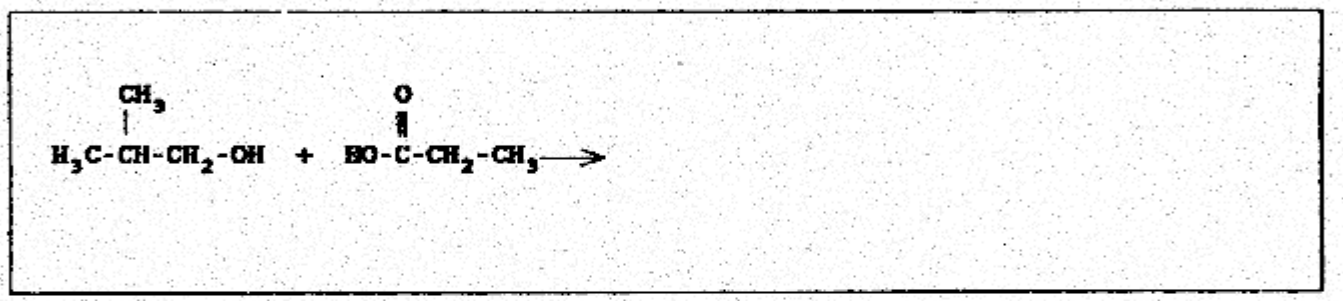
a. Carefully smell samples of cinnamic aldehyde, benzaldehyde, and methyl benzoate. Describe the smell of each compound below. Try to relate the smell to a naturally occurring substance.

(1) Cinnamic aldehyde.

(2) Benzaldeyde.

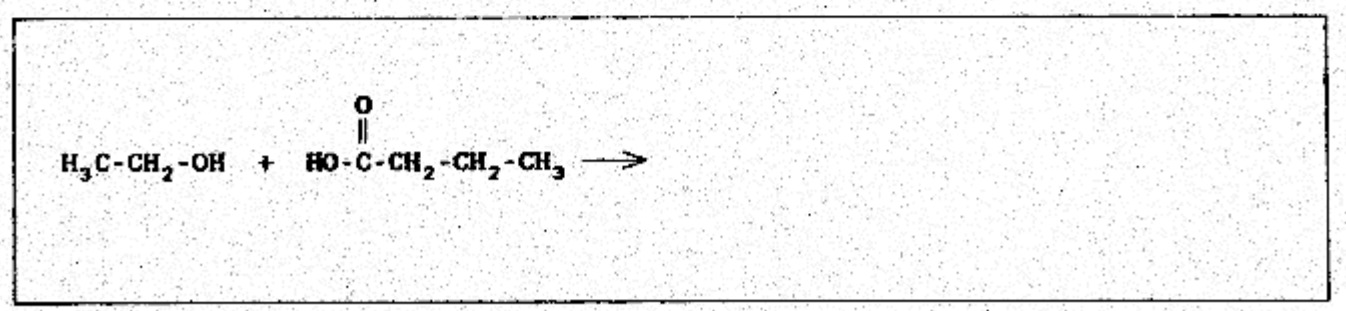
(3) Methyl benzoate.

b. Complete the following reaction for the synthesis of isobutyl propionate:



(1) Carefully sniff a sample of isobutyl propionate. Record your interpretation of the odor below:

c. Complete the following reaction for the synthesis of ethyl butyrate:

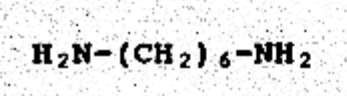


(1) Name the alcohol and acid reactants:

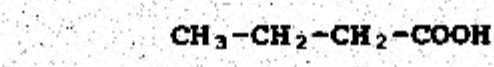
(2) Carefully sniff the odor of ethyl butyrate and describe it below:

**ORGANIC PRELAB EXERCISE**

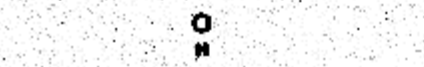
1. Circle the functional groups on the following molecules:



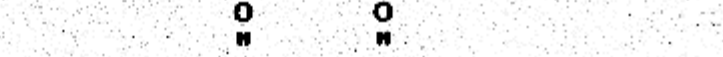
Hexamethylene diamine



Butyric Acid



Benzocaine



Mylar

2. Refer to table 26.4 in your text to identify an ester that could be associated with the following corresponding odor:

| ODOR | ESTER |
|---|---|
| Bananas | |
| Rum | |
| Pineapple | |
| Apricot | |

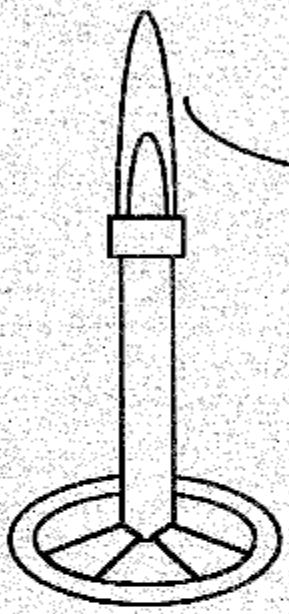
3. Draw the condensation polymerization of nylon from hexamethylene diamine and adipoyl chloride:

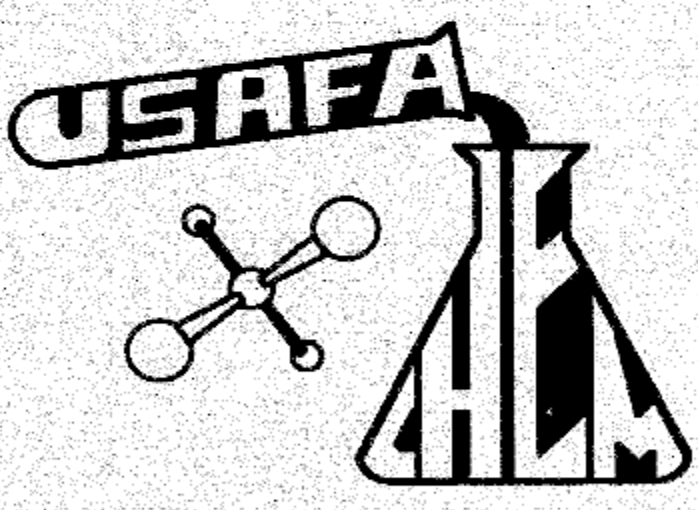
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