

TAMUCC CHEM 1412

General Chemistry II Lab manual (v1.0)

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0- Introduction

This manual contains the guidelines to be followed for the completion of the second General Chemistry Laboratory.

There are twelve sessions of three hours each. The last session is an examination.

Some of the labs might be updated or replaced during the course of the semester.

1- Course Description:

1112.101 is the second semester of General Chemistry Laboratory. It introduces experimental chemistry. The course covers principles and applications of chemical laboratory techniques including preparation and analysis of chemical materials, study of equilibrium, determination of thermodynamic data, study of acid-base reactions, study of oxidation-reduction reactions, data analysis and elementary synthesis. 11 lab reports and one final examination will be due.

The heuristics calls for a strong student involvement and creativity instead of the more traditional cookbook approach. The laboratory is a complement to the lectures and plays an important role in the learning of fundamental concepts.

2- General Student Learning Outcome

- Develop manual dexterity in manipulating apparatus
- Apply mathematics to the study of chemical systems
- Develop ability to solve scientific problems with critical thinking
- Perform volumetric studies
- Calculate and use thermodynamic functions
- Establish the connection between thermodynamics and equilibrium
- Calculate the pH of a system of acids and bases
- Understand the relation between reactivity and oxidation-reduction reactions
- Report the experimental process and data in a lab notebook
- Write comprehensive lab reports

3- Safety Rules

A summary of the mandatory safety rules to be observed follows. A complete presentation of the chemical safety issues at Texas A&M Corpus Christi (points a, b, c, d and e) can be consulted at <http://safety.tamucc.edu/>

- a- Wear ANSI Z-87.1, 1989 goggles at all time in the laboratory. Do not use contact lenses. Be aware of the eyewash station place and use.
- b- Do not ingest any food or drink
- c) Wear clothing providing maximum body coverage including close shoes and gloves. Long hair must be tied. In case of large spill remove the contaminated clothing and use the safety shower.
- d) Never touch nor taste chemicals
- e) Use the hood for any reaction involving gas phase dangerous chemicals
- f) Beware of the breakability of glass
- g) Do not use any electronic device other than required for the experiment
- h) Stow your personal belonging in the designated storage area
- i) In case of an accident, even minor, notify immediately your instructor.

4 – Knowing the chemicals: Material Safety Data Sheet (MSDS)

The Occupational Safety and Health Administration (OSHA) requires that MSDS be available to employees and students for potentially harmful substances handled in the workplace. Commonly used MSDS databases can be accessed through the Environment, Health and Safety homepage at TAMUCC (<http://safety.tamucc.edu/>)

5- Labeling the chemicals: NFPA 704

The National Fire Protection Agency (NFPA), in section 704 of the National Fire Code, specifies a colored diamond system for identifying the hazards associated with materials. The following ranking is used.

Blue – Health

- 0** No hazard other than an ordinary combustible material (peanut butter)
- 1** Only short term irritation and minor residual injury (turpentine)
- 2** Intense exposure can cause temporary incapacitation or residual injury (ammonia)
- 3** Short exposure can cause temporary incapacitation or residual injury (chlorine gas)
- 4** Very short exposure can cause death or major residual injury (hydrogen cyanide)

Red – Flammability

- 0** Will not burn (water)
- 1** Will burn if preheated (olive oil)
- 2** Will burn if moderately preheated or exposed to relatively high temperature (diesel)
- 3** Can be ignited at ambient temperature (gasoline)
- 4** Volatile material burning easily

Yellow – Reactivity

- 0** Stable under fire and not reacting with water (liquid nitrogen)
- 1** Stable unless elevated temperature and pressure (phosphorus)
- 2** Violent chemical change at high temperature and pressure or reacting violently with water (calcium metal)
- 3** Explosive upon contact with an initiating source or water (fluorine gas)
- 4** Can explode by itself at normal temperature and pressure

White – Other Hazards

W hazardous when in contact with water

OX Oxidizer

Non-standard symbols such as corrosive (CORR), acid (ACID), alkaline (ALK), biological hazard (BIOL), poison (POI), cryogenic (CRYO) and radioactive are also used

6-Preparing the experiment

Each experiment requires s preparation including a review of the theory underlying the experiment and a description of the procedure to follow. All the calculations needed to prepare the reactants in the appropriate concentrations and all the relevant chemical equations must be included in such a prelab to be presented in the notebook before the start of the session.

7- Conducting the experiment

- a) The work station and the laboratory equipment must be clean and operational. If such is not the case the instructor must be informed immediately for corrective action. After the experiment is completed all work stations must be cleared and all equipment must be restored.
- b) Reagent dispensers must be kept in their original location. Excess reagent should not be put back in the dispensers but treated as waste.
- c) All material must be weighted on weighting paper or in a container.
- d) Spills must be cleaned after notification of the instructor
- e) Stoppers must be kept in one hand while pouring reagent and put back in place after completion
- f) Waste disposal must comply with the specific instructions given for each session.

8- Managing waste

The best waste management method is to reduce waste at the source. The experimental design follows the principles of green chemistry which includes, if possible, the use of non-polluting chemicals, a minimization of waste and a secure treatment and disposal of the waste that cannot be avoided.

General guidelines and checklists are available on the Campus labs section of the E, H & S home page <http://safety.tamucc.edu/index.php?n=Site>

Furthermore technical information on types of hazardous waste, containers and chemical tables can be found in the Texas A&M University Safety Manual <http://ehsd-online.tamu.edu/documents/TAMUSafetyManual/14-WAST1.HTM>

Chemical wastes are defined as

Chemical components listed in the Texas A&M document

Mixtures containing a listed hazardous waste

Material meeting the definition of one of the following:

Ignitability (flashpoint < 60° C or supports combustion)

Reactivity (e.g., water reactives, cyanides, explosives, unstable chemicals)

Corrosivity (pH < 4 or > 10)

Toxicity (ex. Pesticides, heavy metals, poisons)

Specific waste disposal instructions will be included in the student documentation.

9 – The laboratory notebook:

The notebook, to be graded, is the central piece of the laboratory experience. It is an extensive record of all activities in the lab describing the experiments exactly as they are done and the observations carefully made. It is a record of all the data, their analysis, and the calculations leading to the results to be presented.

The guidelines are as follows.

- The notebook must be bound with numbered pages
- All entries should be recorded in ink and in real time (directly) during the experiment and the calculations. Errors should be crossed and not erased. The notebook will be the source of information allowing the writing of the report. The ultimate criterion for a successful notebook is the ability to repeat the experiment and obtain the same results.
- Each page must be signed and dated

10 -The laboratory report

A lab report will be prepared after each experiment and turned in the following week or as requested. The objective is to learn how to write a scientific paper. A report, like a scientific paper, formulates hypotheses, observes processes, records data, analyzes data, calculates or deduct results and states conclusions. It will include the following fields.

- **Title:** The title might be the name of the experiment or a more elaborate statement. The front page must include your name, the name of the course and the date the report is due. There should be a statement indicating what is your own work in compliance with academic integrity and the shared work authorized by your instructor.

- **Objective:** State the objective in your own words, what scientific principles are being tested, what are the learning objectives.

- **Procedure:** This is where you describe what you have actually done and how you did it. A procedure is a specification of series of actions, acts or operations which have to be executed in the same manner in order to always obtain the same result in the same circumstances.

- **Data collection:** This is one of the most critical portions of the lab report. Without good data recording in the laboratory notebook, completion of the lab write up beyond this point becomes futile. Presentation of data in tables allows easy following of the coming data manipulations. Tables should be clearly labeled as to their content and numbered for ease of referral in the discussion section.

Part of the data may involve making observations (color changes, temperature changes, melting point, boiling point, the physical appearance of a chemical substance, etc.). Sometimes extra observations you make may provide extra clues. Keep your eyes open.

- **Calculation:** One clear example of each different type of calculation should be presented as a check of your work. Do not include pages full of each and every calculation; it just wastes your time and paper. Who wants to read 3 pages of the same calculations with different numbers?

- **Error analysis:** Some estimation of the experimental uncertainty is necessary to help explain the results and to verify if the scientific principle tested holds.

- **Conclusion:** It requires looking at the experimental title, the purpose, the data and calculation sections of the lab report and bringing them all together. Sometimes it involves the comparison of the student's experimentally derived answer to a known literature value. Other times, it requires the student to stress the main point of the experiment.

11- Experiments

Session I: Fundamentals (Part 1) - Atomic chemistry and ideal gases

This is a dry lab and the first unit of two sessions reviewing the knowledge necessary to complete successfully the experiments. After a general presentation the instructor will cover a series of topics pertaining to General Chemistry. Upon completion of the session the students must:

- Know the definitions of element and compound
- Recognize atoms and isotopes and understand the concept of average relative atomic mass
- Know the possible associations between atoms such as molecules, ions and metallic bonds
- Understand the concept of mole and the relation between the mass of a mole and the relative average atomic mass
- Understand the concept of an ideal gas and perform calculations using the ideal gas law.

The instructor will present the five topics as indicated below. Each topical presentation will be followed by an interactive classroom solution of the proposed problems. At the end of the session a quiz will be given to the students.

1- Substance, element and compound

Substance: a form of matter having distinct properties for which the composition (the number and type of basic units present) is constant.

Element: a substance that cannot be separated into simpler entities by chemical means

Compound: A substance made of two or more elements chemically united in fixed proportion

Exercise:

How many elements have been identified?

Give 5 examples of elements and compounds

2- Atom and molecule:

Atom: the basic unit of an element that can combine with other elements. In its simplest representation it is made of protons, neutrons and electrons. The atom is represented by an atomic symbol corresponding to a given number of protons and electrons in the neutral state. There are often several isotopes corresponding to one type of atom depending on the number of neutrons. The known isotopes are listed in the NIST table. An isotope is defined by its atomic number (Z) and mass number (A).

Molecule: an aggregate of two or more atoms held by forces. A molecule is represented by a molecular formula (an expression showing the exact number of atoms of each element in the formula).

Ion: an atom or a group of atoms having a net charge

Exercise:

Describe the atom of carbon-12 indicating the atomic number (Z), the mass number (A), the number of protons, neutrons and electrons of the neutral form

Give 5 examples of diatomic and polyatomic molecules

Give 5 examples of ions.

3- Mass of matter

Atomic mass: the mass of an atom expressed in atomic units (u equals to $1/12^{\text{th}}$ of the mass of one carbon-12 atom)

Only the molar mass of carbon-12 is an integer: the mass of an atom is close to its mass number but not identical. This is due to a phenomenon called mass defect, a loss of some of the baryonic mass into binding energy.

Exercise: find the atomic mass of carbon-12, chlorine-37

http://physics.nist.gov/cgi-bin/Compositions/stand_alone.pl?ele=&all=all&ascii=html&isotype=some

Molecular mass: the sum of the atomic masses of the atoms present in the molecule expressed in atomic units

Exercise: find the molecular mass of the diatomic molecule of deuterium

Average atomic mass: the average of the atomic masses of the different isotopes of an element weighted by their natural abundance on earth

Exercise: calculate based of the relative abundance of the two main isotopes of chlorine the average atomic mass of chlorine and compare your result on the value indicated on your table of elements

4- Unit of amount

Mole: the amount of a substance that contains as many elementary entities as there are atoms in exactly 12 g of carbon-12. This number is determined experimentally to be 6.022142×10^{23} (Avogadro number $N_A = 6.022142 \times 10^{23}$)

Exercise: what is the mass of a mole of carbon-12, a mole of carbon-13?

Molar mass: the mass (in g) of one mole of entities (atom, molecule, etc....)

- If a mole of substance is defined as the number N_A of carbon-12 atoms contained in 12 g, we can say that 12 g of carbon-12 contain N_A atoms of carbon-12. Therefore by definition the mass of 6.022142×10^{23} atoms of carbon-12 (12 u each) is 12 g. In other words ***the molar mass of carbon-12 is exactly 12 g.***
- N_A is a conversion factor between g and u. If there are 6.022142×10^{23} entities of 12 u each in 12 g then there are 6.022142×10^{23} entities of 1 u each in 1 g and 6.022142×10^{23} entities of x u each in x g.

Molar mass of an element:

In a large sample of entities (atoms) we need to use the average mass of the different isotopes as they occur on earth. For instance a mole of Cl would be made of 75.78 % of chlorine-35 and 24.22% of chlorine-37. The mass of a mole of chlorine on earth will therefore be $75.78\% \times (34.969 \text{ g}) + 24.22\% \times (36.966 \text{ g}) = 35.453 \text{ g}$. This is numerically identical to the average atomic mass of chlorine.

Atomic weight and molar masses:

Atomic weight is an old fashion name for the **relative average atomic mass** conveniently presented in some tables of elements. Relative means that it is the average atomic mass divided by its unit (u). Therefore it is unitless and can be used indifferently as the average atomic mass (if the unit is "u") and the **molar mass** (if the unit is "g"). Modern tables refer to molar masses of an element rather than atomic weight. It must be clear that the atomic weight used in chemistry is not properly speaking a weight (in Physics a weight is a force exerted on a body by gravity).

Exercise: calculate the atomic weight of neon from its relative isotopic abundance.

Molar masses of molecules: for practical purpose when working with substances composed of molecules the average molecular mass is calculated from the sum of the average masses present in the molecule. The molar mass of a molecule is thus obtained from the sum of the molar masses of the elements present in the molecule. It must always be remembered that ***molar masses are based on average per isotopic abundance.***

Exercises:

Calculate the molar mass of sodium hydroxide, hydrogen chloride, water.

How many moles are present in 1L of water?

What is the mass of chlorine in 20 g of carbon tetrachloride?

5- Working with gases

Ideal gas equation of state ($pV = nRT$): a relation between temperature, pressure, volume and amount of a hypothetical gas where the gas constant R , which is related to the Boltzmann constant k is a bridge between macroscopic and microscopic chemistry.

Exercises:

A sample of neon at a pressure of 570 hectopascals and a temperature of 29.9°C occupies a volume of 10.1 L. What would be the pressure of the gas sample if the gas is compressed at a constant temperature to a volume of 5.44 L?

Assuming that O_2 is an ideal gas, what is the density of O_2 at a temperature of 0°C and a pressure of 2.25 bars?

Session II: Fundamentals (Part II) - Chemical Reactions

Instructor note:

This is a dry lab and the second unit of two sessions reviewing the knowledge necessary to complete successfully the experiments. Upon completion of the session the students must:

- Understand the meaning of solution and its various components
- Know the main methods of defining a solution quantitatively by the concentration of a solute and be able to modify concentrations by dilution
- Write and balance simple chemical equations
- Solve stoichiometric problems with the reaction table
- Recognize acids and bases, differentiate strong acid/bases from weak acid/bases, understand the meaning of pH, pOH and pK and calculate the pH using the reaction table when required
- Recognize oxidating agents from reducing agents and determine the direction of a RedOx reaction from the cell emf.

The instructor will present the six topics as indicated below. Each topical presentation will be followed by an interactive classroom solution of the proposed problems. At the end of the session a quiz will be given to the students

1- Aqueous chemistry

Mixture: a combination of two or more substances in which the substances retain their identity

Homogeneous mixture: a mixture in which the composition, after sufficient stirring, remains the same throughout. Mixtures can be visually homogeneous but microscopically heterogeneous.

Solution: a microscopically homogeneous mixture with particle size $< 1 \text{ nm}$.

Colloid: a mixture where the particle size is between 1 nm and $1 \mu\text{m}$

Dispersed mixture: a mixture where the particle size is $> 1 \mu\text{m}$.

Solvent: the substance present in larger amount in a solution

Solute: the substance present in smaller amount in a solution

Aqueous solution: a solution containing water as a solvent

Exercise:

Give examples of solutions involving solids, liquids and gases

Classify (solutions, colloids and dispersed) the following visually homogeneous mixtures: water with dissolved sugar, 1M HCl, blood, milk, fog.

2- Measuring the amount of solute in a solution

Concentration: a measure of the amount of solute present in a solution.

Concentration can be expressed in different ways.

Exercise:

Define molarity (M), molality (m), mass fraction (ratio, %, ppm, ppb), mole fraction.

What is the molality of 50% per mass sulfuric acid?

Dilution: the way to decrease the concentration of a given solute to obtain a desired target concentration.

Exercise:

Explain how to prepare 1L of 0.15 M HCl from a 5.3 M solution

3- Chemical reactions

Reaction: a process in which some or several substances are changed into one or more new substances.

Equation: a representation of a chemical reaction using symbols

Exercise:

Write and balance the following chemical equations

Formation of water from molecular hydrogen and molecular oxygen

Combustion of propane producing carbon dioxide and water

Decomposition of potassium chlorate into molecular oxygen and potassium chloride

Formation of aluminum (III) oxide from aluminum and molecular oxygen

4- Reaction Stoichiometry

Reaction table: a chemical spreadsheet to show what happens during a chemical reaction qualitatively and quantitatively. A useful tool that can be used to solve any reaction stoichiometry problem.

Exercise:

The combustion of 10.0 g of ethane with 30.0 g of oxygen produces 10.0 g of water.

What is the percent yield of the reaction? Which reactant will not be completely consumed and what will be the mass of the remaining reactant?

5- Acids and Bases

Brønstedt Acid (aqueous): a substance yielding to an increase in concentration of hydronium ions when put in an aqueous solution.

Brønstedt Base (aqueous): a substance yielding to an increase in concentration of hydroxide ions when put in an aqueous solution.

*Exercise: calculate the pH of a strong acid: 0.1 M HCl
calculate the pH of a strong base: 0.1 M NaOH
calculate the pH of a weak acid: 0.1 HCOOH
calculate the pH of a weak base: 0.1 % NH₃*

6- Oxidizing Agents and Reducing Agents

Oxidizing agent: a substance that can increase the oxidation number of another substance.

Reducing agent: a substance that can decrease the oxidation number of another substance.

*Exercise:
What happens when you put zinc in a solution of hydrochloric acid (1M)?
What happens when you put copper in a solution of hydrochloric acid (1M)*

Session III : Gas Law Relation between Macroscopic Variables

This is the first actual experiment. The instructor will have stressed the importance of the lab preparation in the notebook at the end of session II. A graded quiz at the beginning of the session (counting as part of the 100 points dedicated to the lab) will evaluate the level of preparedness of the students. Students will explore the gas law and its ideal gas form as a relation between macroscopic variables. The relation between temperature and volume will be studied.

Learning objectives:

- a) Understand the concept of an ideal gas, the ideal gas law and the relation between the macroscopic functions involved
- b) Express the gas law equation with units appropriate to a specific problem, know the meaning of STP and SATP and calculate the gas constant in $\text{L}\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ from its value in SI units
- c) Elaborate and follow an experimental procedure to study the temperature dependence of the volume of a given gas at constant pressure
- d) Understand the concept of partial pressure and calculate the volume of a given amount of air from the volume of wet air and the vapor pressure of water
- e) Quantify the deviation of air from an ideal gas
- f) Record in the lab notebook the procedure, experimental data and calculation
- g) Write a report

Experiment Description for the Students

Title: Relation between the volume and the temperature in a gas

Number of experiments required: 2

Objective:

The lab studies the relation between temperature and volume in reference to the ideal gas law $pV = nRT$. While the other parameters (p , n) remain constant we will verify that the change of volume is proportional to the change of temperature.

Tangible deliverables:

Upon review the of scientific background students will deliver the following:

- Notebook summary of the objectives and the required output
- Notebook detailed experimental procedure
- Experiment completion and recording in the notebook of all steps, observed data and calculations
- Comprehensive report.

Background:

The simplest state of matter is a gas. It can be pictured as a collection of entities (molecules or atoms) in continuous random motion. The entities are widely separated and, with the exception of collisions, move in paths that are largely unaffected by intermolecular forces.

The physical state of a gas can be defined by four macroscopic parameters: volume, amount, temperature and pressure. These four variables can be related by an equation of state $p = f(V, n, T)$ in such a way that it is only necessary to specify the value of three variable to know the value of all four and thus describe the system.

The equation of state for an ideal gas is $pV = nRT$ which can be calculated using statistical mechanics. The gas constant is $R = 8.31 \cdot 10^{-2} \text{ L} \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

The law refers to a hypothetical ideal gas and needs to be corrected for real life situations. An ideal gas is a gas with no intermolecular interaction other than perfectly elastic collision. An elastic collision means a collision without any dissipation of energy.

Of course there will always be some intermolecular interaction and furthermore collisions are never totally elastic. Therefore an ideal gas doesn't exist.

Fortunately when a gas is sufficiently diluted it behaves almost like an ideal gas. For the most precise calculation the deviation from ideality can be corrected. For the present experiment we will assume (wrongly) that the gas is ideal and interpret our results accordingly. Generally deviation from ideality will decrease with temperature and density.

The experiment:

You want to prove that the volume of a gas close to ideality is proportional to its temperature. Thus you will need to compare the volume of a gas at two different temperatures. If V is proportional to T ($V = k \cdot T$) then V/T is a constant. You will divide each measured volume by the corresponding temperature. If the values obtained are close then the volume will be considered proportional to the temperature, with an acceptable margin of error and the knowledge that the gas is not ideal.

The procedure:

You will use a 125 ml flask containing air. The two different temperatures will be the temperature of vaporization of water (373.15K) and of fusion (273.15 K). The air contained in the flask will be successively brought to these temperatures by being dipped in boiling water first and then in an equilibrium solution of melting ice. The exact temperature will need to be measured, as the boiling temperature depends on the outside pressure. The flask will first be brought to the high temperature to be measured. How do we know the volume? The simplest way to measure a volume is to fill the container with water (taking account of the experimental set up such as cork and tube) and pour it in a graduated cylinder (this will be done at the end of the experiment in order not to contaminate the gas with water).

To obtain the cold temperature data the flask (carefully closed) containing the air will be brought to the low temperature. At that temperature the air will shrink. You will determine how much it shrunk by filling the remaining volume with water. The volume occupied by the cold air will be obtained by difference between the volume occupied by the hot air (the whole flask) and the water that entered the flask in cold water. Of course the trick is to let the water enter without allowing any air to escape.

Once you have obtained the measurements of both volumes and temperatures you will calculate the ratios and conclude of your success in verifying the gas law by seeing how close the ratios are from each other. The cold air is in contact with water and contains some water vapor, which requires a volume correction to be done taking account of the water vapor pressure at the recorded temperature.

The procedure will be outlined in the notebook before the start of the lab. The atmospheric pressure must be expressed in pascal or bar.

Chemicals and equipment:

The only chemicals involved in the experiment are air and water.

The following equipment can be used: flask, beakers, heater, thermometer, cold bath

Waste management:

There is no waste.

Session IV: Determination of a Molar Mass

The lab consists in the evaporation of a liquid to occupy a certain volume at a certain pressure followed by the condensation of the captured gas in order to obtain its mass and the subsequent calculation of the molar mass using the ideal gas law.

Learning objectives

- Understand the process of phase change
- Understand the concept of mole
- Use the gas law equation to solve for an unknown variable
- Perform an experiment requiring a close monitoring of the experimental field
- Enter the data and calculation in the notebook
- Prepare a lab report.

Experiment description for the students

Objective: The lab is about using the ideal gas law to determine the molar mass of a volatile liquid.

Number of experiments required: 2

Tangible deliverables

Upon review the of scientific background students will deliver the following:

Before the beginning of the lab

- Notebook summary of the objectives and the required output
- Notebook detailed experimental procedure
- Notebook calculation

During the lab

- Experiment completion and recording in the notebook of all steps, observed data and calculations of initial the amount of liquid as a function of the volume of the flask

After the lab

- Comprehensive report.

Background:

The ideal gas law can be used to determine the molar mass of a gas as long as the gas pressure is sufficiently low to assume that there are no interactions other than elastic collisions between the particles constituting the gas.

The experiment:

Students will put in a certain volume (a flask) a sufficient amount of a volatile liquid so that the evaporated gas will occupy the whole volume.

The mass of the gas will then be measured and the molar (MM) mass calculated by applying the ideal gas law $p \cdot V = n \cdot R \cdot T$

Knowing that $n = \text{mass} / \text{MM}$ the gas law can be written
 $pV = (\text{mass} / \text{MM}) \cdot R \cdot T$ and $\text{MM} = \text{mass} \cdot R \cdot T \cdot p^{-1} \cdot V^{-1}$

All variables on the right side of the equation are known.

The pressure is the atmospheric pressure of the day

The volume is the volume to be measured by filling the flask with water (at the end – why?)

The mass of the gas is obtained by quick condensation after evaporation

The temperature is measured with a thermometer in the bath used to evaporate the liquid

R, the gas constant, is not a variable. It is critical to express it in the same units as those of the variable. It is convenient to use $R = 8.31 \cdot 10^{-2} \text{ L} \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

The procedure:

Students will have to decide how much liquid to put initially in the flask. Not enough liquid and there won't be enough gas to fill the whole flask under the atmospheric pressure. Too much liquid and we will produce waste likely to pollute the air.

We can calculate the mass of an ideal gas occupying the volume of the flask using an arbitrary molar mass. The liquid under investigation being very volatile 100g/mol is a reasonable upper limit. Once we have calculated the mass of gas we can multiply it by a large safety factor, for instance 8 times (there will always be some lost liquid).

The evaporation itself tricky because the flask must be cooled at the exact moment when the last drop is evaporated. Too early and we will measure a larger mass than the condensed liquid. Too late and we will lose some of the gas. The temperature needs to be carefully recorded for the gas law calculation. The temperature recorded at the evaporation of the last drop is not the boiling temperature. Students might want to record the boiling temperature at the experimental pressure a clue to the liquid identification.

The flask is closed with aluminum foil pierced with a tiny hole to keep the inside under atmospheric pressure while avoiding the possibility of air input. The condensation can be done under running water or in an ice bath and must be fast while avoiding input of water in the flask.

Chemicals and equipment:

A volatile compound to be identified.

Flasks, beakers, heater, thermometer, scale, pipettes,

Waste management:

The instructor will give specific instruction for the disposal of the volatile liquid in the lab.

Review problems:

The review consists in a series of problems applying the ideal gas law. Emphasis will be on management of units including the difference between SATP and STP as defined by IUPAC.

Session V: Solutions, solubility, molecular interactions

The lab consists in the qualitative and quantitative study of solutions.

Learning Objectives

- Understand solution and homogeneity
- Differentiate solution, solute and solvent
- Understand the process of dissolution
- Observe the solubility and miscibility of solvent-solute combinations
- Explain on the basis of intermolecular interactions the observed solubility and miscibility
- Prepare an aqueous solution of a given molarity of solute
- Prepare an aqueous solution of a given molality of solute
- Convert concentration units expressed in molarity, molality, mass fraction and mole fraction.

Experiment description for the students

Objective

Qualitative quantitative study of solutions. Observation on different types of solutions and discussion of the solubility and miscibility in term of intermolecular interactions. Preparation of solutions of a given concentration and conversion

Tangible deliverable

- Notebook preparation (before the lab) with a description of all chemicals involved including the formula and the relevant data such as polarity and solubility constant
- Notebook presentation of concentration units and the conversion methodology.
- Experiment completion and recording in the notebook of all observations.
- Report containing an interpretation of the observations.

Background:

We define a solution as a homogeneous mixture of two or more substances smaller than 1 nm. We will focus on solutions involving only two substances, with at least one liquid. The liquid is called the solvent and the other substance the solute. In a solution made of two liquids the most abundant liquid is called solvent unless one of the liquids is water in which case the water is always the solvent regardless of its relative abundance. When the solvent is water the solution is called aqueous.

We can define different types of solutions depending of the original states of the compounds involved.

For instance we can identify the following types of solutions:

Original substances		Resulting state	Example
gas + gas	→	gas	air
gas + liquid	→	liquid	soda water
liquid + liquid	→	liquid	ethanol in water
liquid + solid	→	liquid	NaCl, fructose in water
solid + solid	→	solid	brass (Cu/Zn), Solder (Sn/Pb)

Solutions can be characterized in term of the capacity of a solvent to dissolve a solute.

We will work with liquid + liquid and liquid + solid solutions where the solvent will often be water and the solute another liquid or a solid (molecule or ions). We will also observe solutions where the solvent is another liquid than water (for instance cyclohexane).

When the solution contains the maximum possible amount of solute in a given volume and at specific temperature and pressure it is called saturated. Such a maximum amount is called solubility. Solubility is often measured in grams of solute per 100 ml of solvent. For instance the solubility of NaCl in water is 35.6 g/100 ml at 0 °C, 35.9 g/100 ml at 25 °C and 39.1 g/100 ml at 100 °C.

We need to understand the difference between dissolution and dissociation. Dissolution is the process of creating a homogeneous phase from separate substances. Dissociation is the process of splitting a chemical compound into smaller parts (often a crystal into ions).

Dissolution and dissociation are often but not always related. In the case of NaCl, a crystal in the solid state, dissolution involves the separation of sodium and chlorine into ions, the sodium cation and the chlorine anion. The ions are then interacting with water molecules in such a way that they are distributed homogenously. This is a common phenomenon with salts but some molecules do not dissociate in water and yet dissolve. Such is the case of fructose. By convention, when speaking about solubility, chemists indicate the amount of the solute “as you put it in the solvent”

and not what you actually have in the solvent. Properties that depend on the amount of entities actually in the solvent are called colligative properties.

A solution can be unsaturated when it contains less solute than it has the capacity to dissolve. It can also be supersaturated when it contains more solute than at saturation.

A supersaturated solution with water as solvent and a solid solute is always unstable. The solute will eventually come out of the solution by either crystallization (crystals are well formed and often large) or precipitation (small particles).

Solubility as observed in the lab is a macroscopic phenomenon. But how can we explain that some solute dissolve better than others. This is done by the study of microscopic interactions resulting from the forces in presence between molecules.

These forces can be calculated with the tools of electromagnetism and quantum chemistry. For convenience they can be broadly classified into four groups.

- Ion-ion and ion-dipole
- Dipole-dipole (including H-bonding)
- Ion induced dipole and dipole induced dipole
- Dispersion (London)

These intermolecular interactions, responsible for holding together molecules and ions in solids and liquids, play an important role in the solution process. Their study constitute an important part of your General Chemistry II lectures and you should refer to your textbook for an explanation on how they are calculated. For instance the first two types are calculated with the tools of electricity and statistical mechanics while the other two require quantum mechanical calculations.

A solution process can be decomposed into three successive sub processes and their corresponding intermolecular interaction

- Breaking the intermolecular interactions holding the solute together (1)
- Breaking the intermolecular interactions inside the solvent to create a space for the solute (2)
- Creating intermolecular interactions between solute and solvent (3)

Generally a solute will dissolve into a solvent when the energy gained from the attractive intermolecular interactions between solute and solvent compensate the energy needed to separate the solute molecules or ions from each other and create to space needed to introduce the solute into the solvent. In other words the dissolution system must gain energy in the process.

The energy changes occurred during a chemical process is studied with Thermodynamics. Enthalpy (H) is an important component of the energy change

and is well studied because the change of enthalpy is quantifiable under constant pressure.

Enthalpy (H) can help us understand why some solution processes are endothermic while others are exothermic and how to modify the direction of the equilibrium (increase or decrease the solubility).

The difference of enthalpy ΔH of a process is equal to the amount of heat provided to the process at constant pressure. The enthalpy H can be seen as an energy gauge that indicates the amount of heat transferred. For an exothermic process (liberates heat) ΔH is negative. For an endothermic process (absorbs heat) ΔH is positive.

Looking at the three sub processes of a solution, we understand that the first and second steps will require energy while the third step will liberate energy. This generally translates into a positive ΔH_1 and ΔH_2 and a negative ΔH_3 . Therefore if the solute-solvent attraction (ΔH_3) is stronger than the solute-solute interaction ΔH_1 and the solvent-solvent interaction (ΔH_2) the solution process will be exothermic. On the other hand if the solute-solvent attraction is weaker than the solute-solute and solvent-solvent interactions the process will be endothermic.

Should we conclude that solutes would only dissolve in exothermic processes (when the solute-solvent attractions are stronger than the solute-solute attractions)? Not at all! As a matter of fact most solution processes involving a salt in water are endothermic. We know for instance that the dissolutions of NaCl and KNO_3 in water are endothermic and as a consequence the solubility will increase with temperature.

Why then would a solute dissolve in a solvent if its attraction for its own molecule is stronger than the solute-solvent attraction? This is due to the fact that the chemical energy is not only a function of enthalpy but also of entropy. The explanation requires the study of the entropy factor. Entropy is a state function related to dispersal and would generally favor dissolution. The spontaneity of a solution process results often from the competition between the enthalpy factor and the entropy factor at the sub process level.

We can conclude that Enthalpy is useful to understand the transfer of energy as heat but cannot tell us if a solute will dissolve or not. The thermodynamic function indicating if a process will go in one direction or another is the Free Energy (G) which includes two components: Enthalpy and Entropy ($G = H - TS$).

Our general knowledge of the type of interactions along with our understanding of the three sub processes can however give us some idea of the level of solubility.

If two substances with intermolecular forces of similar type and magnitude are mixed they are likely to be soluble.

If both substances are liquids with similar intermolecular interactions they will be miscible (miscibility refers to the ability to be completely soluble in each other). For instance CCl_4 and C_6H_6 are both non polar and miscible. The interactions CCl_4 - C_6H_6 are comparable to the CCl_4 - CCl_4 and C_6H_6 - C_6H_6 interactions.

If a solid salt (NaCl) made of cations (Na^+) and anions (Cl^-) is put into water (a polar solvent), the cations will be solvated (solvation means the surrounding of an ion or a molecule by solvent molecules arranged in a specific manner).

Both examples illustrate a concept known by beginner chemists for many years: "Like dissolves like" and you will be able to verify it in some of your experiments. However the concept is not always true and a more analytical approach must be used to fully understand the dissolution process. Try to explain why barium sulfate, a salt, doesn't dissolve in water, and why beyond a certain concentration a solution of NaCl reaches saturation.

Furthermore we must remember that if the discussion about enthalpy can bring some understanding of the heat exchanged during a process, only the entropy factor will bring a coherent explanation of the entire solution process.

You will perform a series of solubility and miscibility tests as listed in the laboratory textbook and for each couple of substances write your observations. You will then provide an explanation for each case on the basis of intermolecular interactions, decomposition of the solution process into sub processes and enthalpy considerations.

The experiment:

Part A Solubility and Miscibility

You will perform a series a solubility and miscibility tests with some solvents (liquid) and solutes (solids and liquids). In each case you will explain your observations with the intermolecular forces in presence.

You will discuss the exothermicity or endothermicity of a dissolution process and explain why in some case an endothermic process can be spontaneous.

The kinetics aspects will be observed through the comparison of a coarse solid solute with its finely ground form.

The procedure:

Part A Solubility and Miscibility

The solubility and dissolution will be observed in small test tubes.

You will try to dissolve three different solids (sodium carbonate, naphthalene and barium sulfate) in three different solvents (water and cyclohexane). Observations on the nine combinations will be reported in your notebook.

You will then try to mix two of the following liquids: water, cyclohexane and isopropyl alcohol (2-propanol) and report in the notebook the three observations.

Copper (II) pentahydrate is soluble in water and you will compare the kinetics of dissolution for two forms: coarse and finely ground.

Part B Quantitative aspects of solutions

Students will prepare 100.0 ml of 0.5 M and 100.0 ml of 0.5 m aqueous NaCl. They will dilute the 0.5 M solution to obtain 100 ml. of 0.15 M solution and dilute the 0.5 m solution to obtain 10,000 ppm per mass.

Chemicals and equipment:

Water(l), cyclohexane(l), isopropyl alcohol(l), sodium carbonate(s), naphthalene(s), barium sulfate(s) and copper (II) sulfate pentahydrate (crystals), sodium chloride. Test tubes.

Waste management:

Make sure that you do not use more reagent than needed for each observation (2 ml for the liquids and 0.1 to 0.2 g for the solids). All waste, with the exception of water, sodium chloride and diluted isopropyl alcohol, must be disposed in the waste containers available.

Review problems:

Examples of the relation between intermolecular interactions and macroscopic behavior such as solubility, boiling temperature and vapor pressure will be discussed.

Session VI: Titration I Volumetric Analysis

The lab consists in the preparation of reactants in the appropriate concentrations and the use of titration to perform the volumetric analysis of the purity of sodium hydroxide tablets.

Learning Outcome

- Use a problem solving approach to calculate the purity of a sample of NaOH
- Write the relevant chemical equations
- Understand the methodology of titration and define the concentrations of reactants accordingly
- Prepare the reactants in the required concentrations
- Understand the chemistry of pH indicators
- Calibrate and operate a pHmeter
- Perform a titration
- Record the relevant data
- Calculate the purity from the experimental data.

2- Experiment description

Objective:

Prepare a solution of a given concentration; understand titration including acid-base reactions, pH, stoichiometry and molar equivalence.

Tangible deliverable:

Before the lab

- Notebook summary of the objective and procedure
- Notebook determination of the amount of analyte and concentration of titrant

At the lab and after

- Experiment completion and recording in the notebook of all steps, observed data and calculations
- Theoretical calculation of the pH curve and comparison with the experiment
- Comprehensive report with all the calculations including those leading to the determination of initial concentrations.

Background:

Titration is a method of quantitative chemical analysis used to determine the unknown concentration of a reactant in an extensive chemical reaction (in an extensive chemical reaction all the reactants are transformed into product until the limiting reactant runs out). Typically one reactant called the *titrant* of a known concentration and volume will be used to react with a solution of the *analyte* whose concentration is not known.

The titrant can be added to the analyte with a burette and the concentration of the analyte is calculated when the molar equivalence between titrant and analyte is reached. The molar equivalence means that the system resulting from the delivery of a certain number of moles of titrant corresponds to the stoichiometric ratio titrant: analyte. The molar equivalence is obtained from the reaction table with both analyte and titrant fully consumed. For instance in the titration of NaOH (a strong base) as analyte by HCl (a strong acid) as titrant, the stoichiometric ratio is 1:1 and the molar equivalence means that the number of moles of HCl delivered equals the number of moles of NaOH initially present in the solution.

Titration is classified by reaction type (acid-base, oxidation-reduction) and the method used to determine experimentally the molar equivalence point is reaction-specific.

The experiment:

We will do a titration in which the reaction type is acid-base. The equivalence point is characterized by a sharp change of pH which can be followed with a pHmeter. A graph of pH versus concentration will indicate the molar equivalence at the inflexion point of the curve. The point observed experimentally is never exactly the molar equivalence but a “best estimate” and is given the name “end point”. It is easier and cheaper to identify the end point with an indicator instead a pHmeter. Some chemicals such as phenolphthalein will change color when the pH changes sharply between two given values called the indicator’s range. The range of phenolphthalein is 8.3 to 10.0. The shape of a pH curve varies widely with the type of reactants and needs to be taken into account when choosing an indicator.

We will titrate a strong base (NaOH) of unknown concentration with a strong acid (HCl). The objective is to find the purity of NaOH pellets. The pellets are close to purity but not 100 % because NaOH is very hydrophilic and the pellets are likely to be slightly hydrated.

The procedure:

The first part of the laboratory experiment will be the preparation of the reactants and the choice of an indicator. You will need to prepare the analyte, a solution of NaOH, of a chosen concentration and volume and prepare a solution of HCl, the titrant, accordingly. Accordingly means that the end point should be reached after the delivery of manageable volume. If a 50. ml burette is used the volume to be delivered should be between 15. ml and 40 ml. The chosen concentration of NaOH means the concentration of NaOH that you would obtain if the tablets were pure, with the understanding the objective of the titration is to give you a more accurate measurement that you will use to calculate the purity of the tablet.

Acid-base chemistry tells us that the reaction between the hydronium and hydroxide ions is extensive and that the pH of the equivalence point should be close to 7.

You will design a titration procedure indicating the reactants, the equipment, the data to be collected and the calculations. You will then proceed with two or three measurements depending on the precision of the first two.

Your report will review the chemical background, present the data and the result and justify in your error analysis the number of significant figures of your reported concentration.

Chemicals and equipment:

NaOH pellets close to purity, HCl 3M, phenolphthalein

Beckers, flasks, burette, magnetic or manual stir

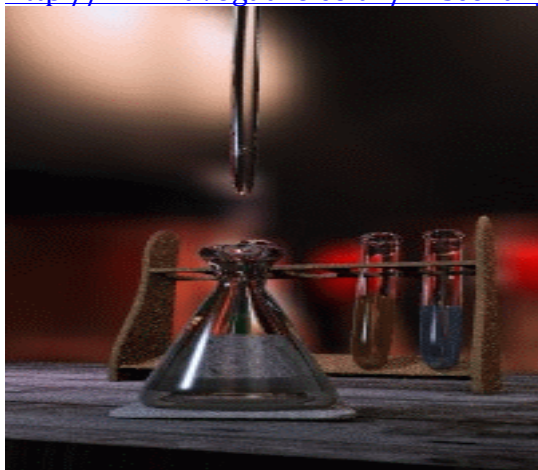
pHmeter

Waste management:

The waste disposal will be handled through neutralization of your excess reactant to a pH between 4.0 and 10.0 and disposal with abundant rinsing.

As a preparation for the lab you may want to practice with

<http://www.avogadro.co.uk/miscellany/titration/titreset.htm>



Review Problems:

The calculations required to prepare the experiment constitute the problems relevant to the session.

Explain why the equivalence point must be at a pH “close to 7.0” and not exactly 7.0.

What is the reasoning behind the choice of the concentration of the titrant?

Session VII: Van't Hoff plot

The lab presents a simple method to calculate standard thermodynamic functions. It is based on the relation between equilibrium constant and standard free energy and on the temperature dependence of the equilibrium constant. With a few approximations related to the narrow range of observed temperatures students will be able to calculate the standard enthalpy, entropy and free energies for the reaction of dissolution of potassium nitrate. Emphasis will be placed on the equilibrium constant as a relation of activities and on the difference between standard and non standard thermodynamic functions.

Learning objectives

- Understand the meaning of enthalpy, entropy and free energy
- Differentiate chemical activity and concentration
- Understand the meaning of standard in thermodynamics and the difference between standard and non standard function
- Discuss the equilibrium constant as a thermodynamic function and a relation between activities
- Measure the equilibrium constant of a given reaction at different temperature
- Calculate with the van't Hoff plot the standard values of enthalpy, entropy and free energy of reaction

Experiment Description

Objective

The objective is to determine experimentally the change of three standard thermodynamic functions for a given chemical reaction. The functions studied are Gibbs Free Energy (G), Entropy (S) and Enthalpy (H). Students will need to understand and explain in their report the difference between the functions, the change occurred by each function during a reaction, and the standard change of that function for a reaction.

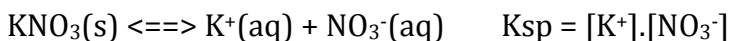
Tangible deliverable:

- Notebook summary of the objective and procedure (before the lab)
- Based on the estimate of temperature at saturation, notebook determination of the volume of initial solution and solute; determination of the incremental amount of water before each step (before the lab)
- Experiment completion and recording in the notebook of all steps, observed data and calculations.

Background

The experimental procedure will allow us to determine the values of the standard changes $\Delta G^\circ_{\text{RXN}}$, $\Delta^\circ S_{\text{RXN}}$ and $\Delta G^\circ_{\text{RXN}}$

The reaction will be the dissolution/dissociation of potassium nitrate



Potassium nitrate is a fertilizer, a rocket propellant, a constituent of gunpowder and a food additive. It is a crystal at room temperature and is moderately soluble in water (360. g/ L at 298.15 K, 1400. g/L at 350.15 K and 2470. g/L at 373.15 K).

The experimental determination will be based on two important thermodynamic equations:

The relation between the equilibrium constant K , the temperature and the standard free energy of reaction for a given reaction (the dissolution/dissociation of potassium nitrate) given by equation

$$K = e^{-\Delta G^\circ_{\text{RXN}}/RT}$$

The relation between $\Delta G^\circ_{\text{RXN}}$, $\Delta H^\circ_{\text{RXN}}$, and $\Delta S^\circ_{\text{RXN}}$,

$$\Delta G^\circ_{\text{RXN}} = \Delta H^\circ_{\text{RXN}} - T\Delta S^\circ_{\text{RXN}}$$

The experiment

It is possible to measure K for different temperatures and determine graphically the value of $\Delta H^\circ_{\text{RXN}}$ by plotting $\ln K$ versus $1/T$.

In order to measure K at different temperatures we will first prepare a fairly concentrated solution that would saturate around 350. K. Saturation will be indicated by the appearance of the first crystal upon cooling. Saturation is a point of equilibrium where $[\text{K}^+].[\text{NO}_3^-] = K$.

As we know the number of moles and volumes of each solution we can calculate K and record the corresponding temperature.

K, as seen in the lecture, is a thermodynamic constant relating activities at equilibrium. In the case of this experiment, the concentrations are taken as an approximation of the activities.

We will then dilute the solution by adding a given amount of water, heat to complete dissolution, and reiterate the cooling process to crystallization. The reaction is endothermic which means that the equilibrium constant increases with the temperature. In other words saturation of the most diluted solutions will be achieved at a lower temperature (the solubility decreases with temperature).

The procedure will be repeated for 5 points and the results will be plotted on a van't Hoff plot ($\ln K$ versus $1/T$).

With a few necessary simplifications you will determine graphically the values of ΔH° and ΔS° for the reaction and calculate the value ΔG° .

To prepare the lab you will:

- Review the thermodynamic study of equilibrium
- Determine the amount of KNO_3 and water needed to have a saturation point around 350. K.
- Describe the experimental procedure allowing the drawing of a van't Hoff plot
- Write the equations needed to calculate the values of the change of standard thermodynamic functions for the dissolution of potassium nitrate.

The lab offers an opportunity to review the relation between Solubility and Thermodynamics and specifically:

- Explore the dependence of equilibrium constant and temperature
- Think about the relationship between K , G , H , S and temperature
- Polish your graphical analysis skill.

Waste

The waste (KNO_3 solution) will be disposed in the available waste bottle.

Session VIII Chemical Equilibrium

The experiment consists in the thermodynamic analysis of an equilibrium and the explanation of the changes occurring when a chemical equilibrium is disturbed.

Learning objectives

- Understand that the equilibrium constant is a unitless function of activities
- Express the relation between standard free energy, the temperature and the equilibrium constant of a reaction
- Understand the difference between a spontaneous reaction and a product oriented reaction and identify the spontaneity of a reaction by comparing reaction quotient (Q) and equilibrium constant (K)
- Calculate with the reaction table the new concentration obtained after quantitative modification of an equilibrium

Experiment Description

Students will observe a series of equilibrium reactions. The direction of the reaction resulting from a change of activity of one of the compounds will be determined and explained by analyzing the dependence of the equilibrium constant on the activities. The direction of the reaction resulting from the input or output of heat to the system will be explained. The quantitative aspects will be studied with the reaction table.

Tangible deliverables

- Notebook preparation including the description of a chemical equilibrium and difference between Q and K (before the lab)
- Observations and pH calculation (buffer)
- Scientific explanation of the observations and comparison with intuitive approach
- Preparation of a comprehensive report.

Background

Chemical Equilibrium is state in which all macroscopic properties remain unchanged.

At the microscopic level matter and energy continue to interact but the macroscopic nature of equilibrium makes it particularly suitable to classical thermodynamic study.

When a chemical reaction has reached equilibrium none of the macroscopic parameters change (amounts, temperature, pressure, volume), all activities (approximated by concentrations or partial pressures) remain the same, while at

the microscopic level reactant molecules continue to form products and product molecules continue to form reactants.

Most chemical reactions lead to equilibrium, to some extent, meaning that, depending on the conditions, they can proceed either forward or backward.

Experiments showed that when a chemical reaction involving diluted solutes, or gases at a low pressure, is at equilibrium and at a constant temperature, the concentrations of reactants and products reach a certain ratio called the equilibrium constant.

In fact the equilibrium constant is a ratio of activities. Activities are complex functions but, in close to ideal solutions (very diluted) and close to ideal gases (low pressure) activities can be approximated by concentration or partial pressure.

In other words when the solution is very diluted, the activities can be replaced by the concentrations divided by the concentration unit to obtain a dimensionless equilibrium constant. For low-pressure gases, activities can be approximated by the partial pressure divided by the pressure unit. For pure solids and liquids (including the solvent in a diluted solution), activities are equal to 1.

As an example, in the dissociation of an acid in water, the solvent does not enter in the expression of the equilibrium constant. Indeed the equilibrium constant of the reaction



$$K_a = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

where $[\text{CH}_3\text{COO}^-]$ means $[\text{CH}_3\text{COO}^-]/1\text{M}$ which is an approximation of the activity of CH_3COO^- in the solution and the activity of the solvent (water) equals 1.

A more general expression of K must be used for more complex chemical reactions such as when some stoichiometric coefficients have values different than 1 or when the reaction includes gases.

For the generic reaction



$$K = a_C^{\gamma} \cdot a_D^{\delta} / a_A^{\alpha} \cdot a_B^{\beta}$$

With a_A = the activity of reactant A at equilibrium

For the reaction $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

$$K_a = a_{\text{CH}_3\text{COO}^-(\text{aq})} \cdot a_{\text{H}_3\text{O}^+(\text{aq})} / a_{\text{CH}_3\text{COOH}(\text{aq})} \cdot a_{\text{H}_2\text{O}(\text{l})}$$

Using the following approximations of the activities

Pure solid	$a = 1$
Pure liquid, solvent	$a = 1$
Solute	$a = [\text{solute}] / 1\text{M}$
Gas	$a = p_{\text{gas}} / 1 \text{ bar}$

$$K_a = [\text{CH}_3\text{COO}^-] \cdot [\text{H}_3\text{O}^+] / [\text{CH}_3\text{COOH}]$$

$[\text{CH}_3\text{COOH}]$ indicates the concentration of CH_3COOH divided by 1M at equilibrium

The equilibrium constant K is a particular value of the reaction quotient Q. This means that Q, like K is the ratio of products over reactants. The difference is that Q can take any value and depends only of what amount is present at a given time while K has only one possible value for a given reaction at a given temperature.

Comparing Q and K is very useful because a reaction away from equilibrium will always tend to go toward equilibrium which means modify the ratio of products over reactants in order for Q to reach K. By comparing Q and K we can figure out the direction in which the reaction will proceed spontaneously.

K does not indicate spontaneity (in fact it only indicates the spontaneity of an hypothetical reaction where the reactants in standard condition are entirely transformed into products in standard conditions). But K gives us a valuable information indicating if the reaction is product oriented or reactant oriented. The meaning of product oriented is that at equilibrium there are more products than reactants. A product oriented reaction has a large K while a reactant oriented reaction has a small K.

Thermodynamically speaking the value of K is related to $\Delta G^{\circ}_{\text{rxn}}$, the change of standard Gibbs Free Energy for the reaction where the reactants in standard condition are entirely transformed into products in standard conditions

$$K = e^{-\Delta G^{\circ} / RT}$$

The thermodynamic expression for K shows two important features:

- A relation between the equilibrium constant and the temperature as was explored in the previous lab on the van't Hoff equation
- The reason why the value of ΔG° indicates if the reaction is product oriented or reactant oriented. If $\Delta G^\circ < RT$ the equilibrium constant K is small and the equilibrium is product oriented; and if $\Delta G^\circ > 0$ the equilibrium is reactant oriented. By product oriented we mean that at equilibrium there will be more product than reactant.

As explained in more details in the lecture in order to figure out the direction in which the reaction will proceed spontaneously the value of ΔG must be calculated. ΔG of a reaction is the change of Gibbs Free Energy for a reaction occurring in non standard condition and is expressed by an equation where a term expressing the deviation from standard conditions is added **$\Delta G = \Delta G^\circ + RT \ln Q$**

Equilibria can be simple or multiple as well as homogeneous and heterogeneous. We will study a few simple homogeneous equilibria and see how the reaction quotient always moves toward the equilibrium value. By comparing Q to its equilibrium value (K) it is possible to find in which direction the reaction will proceed. A similar conclusion can be reached with the calculation of the change of Gibbs Free Energy for the reaction (ΔG).

The behavior of a reaction away from its equilibrium was described qualitatively in the XIXth century by the French engineer Henri Louis Le Châtelier: "if an external stress is applied to a system at equilibrium the system will adjust in such a way that the stress is partially offset as the system reaches a new equilibrium". Interestingly the observation applies not only to concentration and pressure but also to volume and temperature. It is however not useful in quantitative analysis because it lacks the theoretical background required for calculations.

2- The Experiment

We will study the three following reaction systems:

- $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- $\text{CoCl}_4^{2-}(\text{eth}) + 6 \text{H}_2\text{O}(\text{eth}) \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{eth}) + 4 \text{Cl}^-(\text{eth})$
- $\text{NH}_4\text{Cl}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$

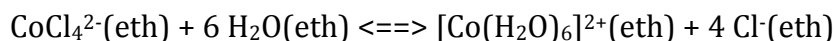
a) Dissolution of acetic acid (1M) in water (monitored by methyl orange)

The experiment is performed in a small flask

- 1- Check the acidity of 50.0 ml 1.0 M acetic acid with a few drop of methyl orange
- 2- Add 0.02 moles of potassium acetate
- 3- Observe and explain the change of color
- 4- Calculate the pH of the solution
- 5- Heat the solution and record your observation
- 6- Cool the solution and record your observation
- 7- Refer to the relation between equilibrium constant and standard free energy of reaction to decide if the reaction is exothermic or endothermic
- 8- Compare your answer to (7) with the Principle of Le Châtelier

b) hydration of cobalt tetrachloride in ethanol

The experiment is performed in a small test tube



- 1- Write the equilibrium constant as a function of activities
- 2- Record your observation upon addition of water and explain the change
- 3- Record your observation upon addition of HCl and explain the change
- 4- Record your observation after addition of more water and explain the change
- 5- Heat the solution and record your observation
- 6- Cool the solution and record your observation
- 7- Refer to the relation between equilibrium constant and standard free energy of reaction to decide if the reaction is exothermic or endothermic
- 8- Compare your answer to (7) with the Principle of Le Châtelier

c) Dissolution of ammonium chloride in water

The experiment is performed in a small test tube

- 1- Dissolve ammonium chloride and record any change in temperature
- 2- Heat the saturated solution and record your observation
- 3- Cool the saturated solution and record your observation
- 4- Refer to the relation between equilibrium constant and standard free energy of reaction to decide if the reaction is exothermic or endothermic
- 5- Compare your answer to (4) with the Principle of Le Châtelier

Waste

All waste will be discarded in the appropriate waste container

Session IX: Chemical Analysis of a Titration

Students will titrate a solution of hydrochloric acid with a solution of sodium hydroxide previously standardized with a primary standard (KHP). The standardized titrant will be diluted to 0.100 M and the analyte diluted accordingly for an effective measurement. After an initial titration aimed at finding the approximate concentration of the analyte, a precise pHmeter titration curve will be performed..

Learning Objectives

- Understand the acid-base properties of water and the meaning of pH
- Understand the reaction of a strong acid with a strong base
- Prepare the reactants in concentrations appropriate for an effective titration and standardize the titrant
- Perform a titration with the proper adjustment of delivery rate
- Monitor the change of pH with a pHmeter, draw a curve of pH versus volume of titrant delivered and associate the equivalence point with the inflexion point
- Analyze the pH versus delivered volume curve quantitatively stressing the relation between volume delivered, amounts and concentrations
- Calculate the pH at several points on the curve.

Experiment description

Objective

Qualitative and quantitative analysis of the titration of a strong acid by a strong base. The acid-base chemistry will be reviewed. The titration curve will be drawn and discussed. The experimental curve will be compared with theoretical calculations of the pH at several significant points.

Tangible deliverable

- Notebook presentation of the acid-base reactions involved (before the lab)
- Notebook presentation of the experimental procedure (before the lab)
- Preparation of the solution of titrant before standardization and calculations
- Data of standardization, calculations and results
- Dilution calculations and results
- Determination of the equivalence point
- Data of the titration followed with the pHmeter
- Plot of the pH versus volume delivered (titration curve)
- Calculation of pH for several points on the curve
- Comprehensive report.

Background

The titration of a strong acid by a strong base, or a strong base by a strong acid, is a simple neutralization. The active reactants are the protons (hydronium ions) and the hydroxide ions reacting with each other to generate water. At neutralization, meaning that all the hydronium and hydroxide ions have combined, we are left with only water and a neutral salt. The pH corresponds to the small amount of hydronium present in pure water (10^{-7}M) due the autodissociation reaction. The titration curve (pH versus volume of titrant delivered) is almost symmetrical because first we decrease the concentration of the ion in the analyte and after neutralization we increase the concentration of the ion from the titrant. Around neutralization there is a sharp change of pH with an inflexion point at equivalence. It is such a sharp change that allows the determination of the equivalence with an indicator changing color in a certain pH range. The titration is typically used to find the concentration of a solution. Although there are many different types of titrations (such as oxidation-reduction) we cover only the acid-base.

The calculation of the pH at different points of the titration requires only the calculation of the concentration of hydronium, which is easily done with the reaction table as covered in the first lab. Once we have the concentration of hydronium we can calculate the pH, the negative of the decimal logarithm.

Outline of a procedure

- Prepare a solution of titrant (NaOH) (one solution for the lab)
- Standardize the titrant with KHP
- Prepare the solution of analyte to be titrated (one solution for the lab)
- Titrate the analyte (indicator monitoring)
- Repeat the titration with enhanced precision (volume delivery) and pHmeter monitoring
- Calculate the exact concentration of analyte
- Plot the experimental titration curve from $V = 0$ to $V = 2 \cdot V_{\text{eq}}$
- Calculate the pH at the following points: $V = 0$; $V = V_{\text{eq}}/2$; $V = 0.9 \cdot V_{\text{eq}}$; $V = V_{\text{eq}}$; $V = 1.05 \cdot V_{\text{eq}}$; $V = 1.5 \cdot V_{\text{eq}}$; $V = 2 \cdot V_{\text{eq}}$
- Compare the calculated points with the experimental curve.

Waste

All chemicals will be neutralized to $4 < \text{pH} < 10$ and discarded with abundant rinsing.

Session X Titration of a weak acid

The third titration will introduce the enhanced complexity of acid-base chemistry with weak acids and weak bases. Students will learn to recognize the species present in a solution and to calculate the pH accordingly.

Learning Objectives

- Understand the chemistry of weak acids and weak bases in aqueous solutions
- Understand the mechanism of action of a buffer
- Calculate the pH resulting from the reaction of a strong base with a weak acid
- Identify the acid from the shape of the titration curve.

Experiment description

Objective

Perform the titration of a weak acid with a strong base. Determine the species from the acid dissociation constant (K_a) and the concentration from the equivalence point. Calculate a series of points on the titration curve and compare the experimental and theoretical curves.

Tangible deliverables

- Notebook presentation of the acid-base reactions involved (before the lab)
- Notebook presentation of the experimental procedure (before the lab)
- Preparation of the solution of titrant before standardization and calculations
- Data of standardization, calculations and results
- Dilution calculations and results
- Determination of the equivalence point
- Data of the titration followed with the pHmeter with the proper adjustment of delivery rate
- Plot of the pH versus volume delivered (titration curve)
- Calculation of pH for several points on the curve
- Comprehensive report

Background:

A weak acid will react extensively with a strong base meaning that it will be transformed into its conjugate base. The titration curve will however be different than in the case of a strong acid because the acid base system will consist of more species than the hydronium and hydroxide ions. A theoretical calculation of the reaction curve will require a chemical understanding of equilibrium acid-base chemistry including buffers.

Before the beginning of the titration the solution consists of a weak acid and water. The pH can be calculated with the reaction table from the initial concentration and the K_a . Both can be determined from the titration curve.

The nature of the weak acid is known, it is acetic acid. The K_a is 1.8×10^{-5} . A first titration with phenolphthalein as an indicator will determine the concentration. Once we know the K_a (and therefore the pK_a) and the concentration of the analyte, as well as the concentration of the titrant (determined by standardization with KHP) we will be able to calculate the pH for any amount of titrant delivered.

Acid-base chemistry combined with the use of the reaction table tell us that the titration curve is made of two distinct zones separated by the equivalence point.

The first zone, between the initial solution and the equivalence, is a buffer zone because it is made of a weak acid and its conjugate weak base. The pH at any point can be calculated with the Henderson-Hasselbalch equation. The respective concentrations and amounts (in number of moles) can be calculated with the reaction table. Students should be able to decide when to use the reaction table in number of moles or in concentration and how to do the conversion of one to the other. There is an inflexion point in that first zone at exactly $\frac{1}{2} V_{eq}$ and the delivery during the titration must be adjusted accordingly.

The titration around the equivalence point is similar to the previous experiment with a strong acid and a strong base, with the difference that now the pH at equivalence is not going to be 7. To calculate the pH students will understand that at equivalence all the acetic acid has been transformed into acetate and that the pH will therefore be the pH of a weak base at the new concentration (the concentration changed because the volume of the solution changed).

The pH in the third zone can be calculated from the concentration of the strong base. This is due to the fact that in an aqueous solution containing a strong base and a weak base the pH is exclusively defined by the strong base. The explanation can be seen from a look at the reaction of the weak base with water in the presence of a common ion.

Outline of a procedure

At the lab level

- 1- Prepare from pellets a solution of sodium hydroxide approximately 0.1 M and find the precise concentration by standardization with KHP
- 2- Prepare a solution of acetic acid approximately 0.1 M

Each group

- 3- Titrate (phenolphthalein) the acetic acid to find the concentration
- 4- Titrate (pHmeter) the acetic acid
- 5- Plot the experimental titration curve from $V = 0$ to $V = 2 \cdot V_{eq}$
- 6 - Calculate the pH at the following points: $V = 0$; $V = V_{eq}/4$; $V = V_{eq}/2$; $V = 0.75V_{eq}$; $V = 0.9 \cdot V_{eq}$; $V = V_{eq}$; $V = 1.05 \cdot V_{eq}$; $V = 1.5 \cdot V_{eq}$; $V = 2 \cdot V_{eq}$
- 7- Compare the calculated points with the experimental curve.

Waste

All chemicals will be neutralized to $4 < \text{pH} < 10$ and discarded with abundant rinsing.

Session XI Oxidation –Reduction reactions

Students will build a voltaic cell with three combinations of half-cells in standard thermodynamic conditions. The cell's emf will be measured and compared to tabulated data of half-cell reduction potentials. The reduction and oxidation reaction will be identified and the anode and cathode determined.

In the second part of the lab students will dissolve metallic copper in nitric acid and, after a few chemical transformation reduce the copper cation with zinc in an acid environment. The reduction of copper by zinc and the oxidation of zinc by both copper and protons will be explained.

Learning objectives

- Understand oxidation- reduction reactions
- Build a voltaic cell and measure the emf of several oxidation-reduction couples
- Compare the observation with tabulated data
- Perform a series of chemical reactions involving copper and interpret the oxidation-reduction data in term of tabulated half-cell reduction potential.

Experiment description for the students

Objective

The main objective is the qualitative and quantitative understanding of oxidation-reduction reactions. Students will investigate the process of oxidation-reduction with a voltaic cell and two electrodes, one electrode being reduced while the other is oxidized. Measurements of the electromotive potential with a voltmeter will be compared with tabulated thermodynamic data. A series of chemical reactions involving copper, hydrogen and zinc will then illustrate the relation between thermodynamics and spontaneity.

Tangible deliverable

- Notebook summary of oxidation-reduction mechanism (before the lab)
- Description of the voltaic cell (before the lab)
- Completion of the two parts of the experiment and recording of the data in the notebook
- Comprehensive lab report with a chemical interpretation of the experiment including an explanation of the dissolution of copper with nitric acid but not sulfuric acid and why both sulfuric acid and copper will oxidize zinc.

Background

Students will need to review oxidation-reduction chemistry and particularly:

- ***Oxidation state***: the hypothetical charge of an atom if all bonds to atoms of different elements were ionic
- ***Oxidation***: the increase of the oxidation state of an element
- ***Reduction***: the decrease of oxidation state of an element
- ***Reduction (redox) potential***: a measure of the tendency of a chemical species to be reduced (acquiring electrons for a metallic ion is one type of reduction)
- ***Standard reduction potential (E°)***: a measure of the tendency of a chemical species to be reduced in standard thermodynamic conditions in a reaction where one of the electrodes is the standard hydrogen electrode (SHE)

The relative reactivities of different half reactions can be compared in order to predict the direction of the electron flow. A higher E° means that there is a higher tendency for the reduction to occur.

The table of half-cell reduction potential will explain the direction of the oxidation-reduction reactions in the experiment.

The experiment

In the first part of the experiment students will build a voltaic cell by combining two beakers out of three containing the following solutions: $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$. Each solution will be 1.0 M. There will be three possible combinations. The two beakers will be linked by a salt bridge made of a U tube containing KNO_3 blocked by cotton at the extremities and connected with a wire between the electrode provided (copper, zinc and lead). The voltage difference between the electrodes will be measured with a voltmeter.

Outline of a procedure

Part I

- 1) Drop the Zn metal strip in the beaker with the $\text{Zn}(\text{NO}_3)_2$ solution, the Cu in the $\text{Cu}(\text{NO}_3)_2$ solution and the Pb in the $\text{Pb}(\text{NO}_3)_2$ solution. Electrodes must be prepared by rubbing until shiny with a ball of steel wool.
- 2) Fill the U tube to the top with a solution of KNO_3 .
- 3) Close both ends of the U tube with cotton balls.
- 4) Place the Zn beaker and Cu beaker next to each other and connect them with the bridge.
- 5) Turn on the voltmeter and connect it to the electrodes after calculating which pole will be the anode and which pole will be the cathode. The voltage reading should be positive. Record the voltage.
- 6) Remove the bridge and voltmeter clips. Repeat steps 4) and 5) for the beakers Pb and Cu. Record the voltage. In case of leak steps 2 and 3 might have to be repeated.
- 7) Remove the bridge and voltmeter clips. Repeat steps 4) and 5) for the beakers Zn and Pb. Record the voltage. In case of leak steps 2 and 3 might have to be repeated.

Part II

- 1- Oxidize approximately 0.4 g $\text{Cu}(\text{s})$ into $\text{Cu}^{2+}(\text{aq})$ in 3.0 ml concentrated HNO_3 . Use a 250.0 ml beaker. The reaction is producing a very toxic gas and should be performed under a hood. Add 10.0 ml of DI water.
- 2- Transform the copper ion into $\text{Cu}(\text{OH})_2(\text{s})$ by addition, while stirring, of NaOH 6M drop by drop until the mixture becomes basic to be checked with litmus paper.
- 3- Converts $\text{Cu}(\text{OH})_2$ into CuO by gently boiling (4 min) the mixture to which 80 ml. of distilled water are added.

4-Cool and filter; you may use a small amount of distilled water to transfer the last trace of solid CuO

5- Rinse residue (three times with 5. ml hot water)

6- Dissolve by repetitive filtration the residue in 10. ml 3M H_2SO_4 and rinse filter

7- Add 2 g of solid zinc Zn(s) to the acid solution to reduce the copper. Oxidize the remaining zinc by adding small amounts of sulfuric acid. Decant the copper and dry.

8- Weight the dried copper, compare with the initial amount (the drying process cannot be fully completed in the lab time) and discuss the results.

Report:

- Write all relevant equations
- Find the relevant half-cell potentials
- Identify the oxidation-reduction reactions and explain their direction
- Report the recovered mass of copper and indicate the percent yield. If the percent yield is over 100 % explain the possible errors.