The Chemistry 223 Companion

Lab Manual, Problem Sets, Lecture Slides and Learning Resources

Dr. Michael A. Russell
Mt. Hood Community College
Spring 2025

Welcome to Chemistry 223!

My name is **Dr. Michael Russell** and I am pleased that you have decided to take Chemistry 223 with me this quarter. I look forward to an exciting term with you!

Here are some hints on how to get the most out of the ***Chemistry 223 Companion***:

- Glance over the **Table of Contents** that follows this introduction. The Table of Contents lists the respective page numbers for each of the sections.

- If you need it: information on **how to construct a graph** can be found in the lab section (with a Roman number "***I***" leading.) A handy **pictorial guide to common glassware**, a ScienceNotes.org **Periodic Table** and a **parts per thousand handout** follow shortly afterwards. The **labs** we will be performing this quarter follow.

- The **problem sets** and **Exam Prep worksheets** that we will use this quarter follow the lab section. They are listed with a Roman number "***II***".

- A printed version of the **Lecture slides** that will be covered this quarter can be found next. The PowerPoint notes use a Roman number "***III***" followed by the Chapter number, then the page number. For example, ***Page III-5-3*** would refer to a PowerPoint note (the "***III***") in Chapter ***5*** (the "***5***"), and the "***3***" refers to the ***third*** page of notes for Chapter 5.

- **Lecture handouts** follow the lecture slides and augment difficult concepts discussed in lecture. The numbering system is similar to the PowerPoint slides system but with a "**IV**". For example, ***Page IV-5-1*** would refer to a Lecture Handout (the "***IV***") in Chapter ***5*** (the "***5***"), and the "***1***" refers to the ***first*** page of lecture handouts for Chapter 5.

- Finally, the **Concept Guides** (which are useful worked examples relating to each of the chapters studied this quarter) might prove useful – they begin with a Roman number **V**. Also, **practice problem sets** (which include answers at the end; they begin with a Roman number **VI**), various **quizzes with answers** (which begin with a Roman number **VII**) and finally **sample quizzes and exams** (with answers, they start with a Roman number **VIII**) follow shortly after. Note that additional quiz and exam testing resources are available on the CH 223 website (http://mhchem.org/223/classroom/qe.htm).

If you have questions throughout the quarter, please do not hesitate to contact me using the contact information below. Good luck with your studying!

Peace,

Dr. Michael Russell
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http://mhchem.org/223 - *CH 223 website*
(503) 491-7348 - *phone*
AC 2568 - *office*

CHEMISTRY 223 TABLE OF CONTENTS

CH 223 Laboratory Experiments - *http://mhchem.org/lab223*

CH 223 Labs - *http://mhchem.org/lab223*

CH 223 Problem Sets and Exam Prep Worksheets - *http://mhchem.org/pset223*

CH 223 Lecture Slides - *http://mhchem.org/ho223*

CH 223 Handouts - *http://mhchem.org/ho223*

Chapter Thirteen:

Chapter Fourteen Part I:

Chapter Fourteen Part II:

Chapter Fifteen:

Chapter Sixteen:

Chapter Seventeen:

Chapter Eighteen:

Chapter Nineteen:

CH 223 Concept Guides - *http://mhchem.org/ho223*

CH 223 Practice Problem Sets and Quizzes *(with answers)* - *http://mhchem.org/223*

More sample quizzes and exams online - http://mhchem.org/223/classroom/qe.htm

Laboratory Safety & Etiquette

Safety is of utmost importance. Work in the laboratory should be a safe experience. It will be safe, however, only if certain safety precautions are followed without exception. Safety is up to you. Everyone working in the chemistry laboratories must follow the following rules. Your instructor will discuss specific safety precautions relevant to each experiment during the pre-lab lecture. Do not hesitate to consult with your instructor if you have questions regarding any safety precautions. Failure to observe laboratory safety rules and procedures may result in injury to you or to fellow students. Students who do not follow these safety rules (including proper attire) will be asked to leave the laboratory. Repeat offenders may be dropped from the course at the discretion of the instructor.

1. **Appropriate attire:** Appropriate protective clothing must be worn at all times while in the laboratory. It is a good idea not to wear your best clothing to lab since many chemicals can stain, bleach or generate holes in your clothing.
    a. **Safety goggles** approved by the chemistry department must be worn at all times, even if you are wearing prescription glasses. Contact lenses are not recommended in the lab. Various fumes may accumulate under the lenses and injure your eyes. You are responsible for bringing your own pair of safety goggles to lab each week. Students who borrow safety goggles from the instructor will have points deducted from their lab. Students who fail to wear their safety goggles will be reminded once and have points deducted. The second time a student is seen without safety goggles on during a lab period, the student will be asked to leave the laboratory.
    b. **Shirts** must cover the entire upper torso, including the midsection and upper chest area and should be long enough to tuck inside your pants. Cotton t-shirts are fine. Tank tops, scooped neck tops, leotards, sleeveless blouses and tops made of sheer material are not allowed.
    c. **Pants and skirts** must be at least knee length. **Shoes** must be flat-soled and cover the entire foot. Socks must be worn with shoes. Sandals, open-toe shoes and high heels are not permitted.
    d. **Long hair** (shoulder length and longer) and billowy clothing must be tied back while working in the lab.

2. **Food and Drink:** NO food or drink will be allowed in the laboratory. This includes coffee, water, candy and chewing gum.

3. Working in the laboratory without an instructor present is strictly forbidden. Students must work in instructional laboratories only during regularly scheduled lab periods and then only when supervised by a member of the faculty.

4. Do not perform any unauthorized experiments. If you have an idea for improving an experiment or for a new experiment, consult with your instructor.

5. Wash your hands after every experiment and each time your hands come in contact with chemicals.

6. **Scales:** Never weigh reagents or chemicals directly on a balance or scales. First weigh an empty container or weighing paper, then press tare or "re-zero" to set the mass reading to zero. Then add your reagent to the container or weighing paper and re-weigh. Balances are expensive! Clean any spills immediately! Replace caps on bottles and return to cart when complete.

7. **Fume hoods** should be used when performing experiments that generate an objectionable gas.

8. **Working With Chemicals:**
    - a. Never smell or taste anything in the laboratory unless specifically directed by your instructor. Many chemicals are poisons. Use your hand to waft the odor to your nose.
    - b. Always **read the label** on all chemical bottles and waste bottles. If you see the wrong chemical, you may have a serious explosion. If unsure, consult with your instructor.
    - c. Do not take chemical bottles to your lab bench unless directed by your instructor. Pour the approximate amount you need from the bottle into a small container and take this to your bench.
    - d. Always use a metal spatula or scoopula to transfer solid chemicals. Do not use your finger to transfer chemicals. This will directly expose you to the potential hazards of the chemical and might contaminate the remaining chemical in the container.
    - e. Do not put excess reagent back into the original bottle. There is always a chance of contaminating the original sample. Ask your instructor how to properly dispose of excess chemicals.
    - f. Do not put pipets directly in any reagent bottle. This might result in contamination of the remaining liquid in the bottle. Never mouth pipet any liquid in the lab.
    - g. Keep the lids and caps on the chemical bottles. Put the lids back on as soon as you are finished dispensing the material. Many chemicals are sensitive to light or to moisture in the air.
    - h. When diluting concentrated acids or bases, add the acid or base slowly into water. Never pour water into acid. The heat generated from adding water to a concentrated acid or base solution can cause the solution to splatter or shatter the glass.

9. **Waste:** Dispose chemical waste in designated containers. Only flush chemicals down the sink if instructed by your instructor. Never pour organic waste down the drain. The waste containers are in the hood for each experiment. Read labels on waste containers to be sure to dispose of waste in the proper container. Disposing waste in the wrong container can generate an unwanted (and unexpected) chemical reaction!

10. **Spills:** Clean up any spills immediately and dispose of the spilled material properly. Check with your instructor on the proper way to clean up any material that you spill.

11. **Chipped or broken glassware** should be thrown in the glass waste container. Report broken glassware to your instructor so that it can be replaced.

12. **Hot objects** will burn! Do not pick up hot objects with your fingers. Use tongs or hot pads. Hot glass will crack if run under cold water. Allow heated glass sufficient time to cool.

13. **Accidents and Emergencies:** Report all injuries and accidents, no matter how minor, to your instructor immediately. Know the location of the fire extinguishes, fire blankets, safety showers, and eyewash stations. Familiarize yourself with two different exits from the lab, in the event of an emergency situation. Accidents are usually minor, but it is best to be prepared for serious trouble.

14. **Be aware of your classmates!** Are they obeying the safety rules? A nearby accident may not hurt or harm him/her but may injure you!

15. Above all else, **ask the instructor if you have any safety related questions!**

Information on Graphs

Graphs: Whenever you create a graph for a chemistry lab, keep the following points in mind:

- If creating a graph by hand, use a large portion of the graph paper to create your graph; small graphs can easily misrepresent data and/or trendlines. If using a computer program like Microsoft Excel, use large graph sizes when creating lab reports (up to the size of one complete page.)
- Plan ahead! Make sure all the data points will fit on the graph but will not be too crowded together horizontally or vertically. Again, use as much of the graph paper as possible when constructing your graph.
- On the vertical axis, label the quantity that is being plotted (i.e. "Time") <u>and</u> put its units in parentheses (i.e. "(seconds)". Do the same on the horizontal axis.
- If you are drawing a **best-fit line** through the data points, do ***not*** connect the dots! Instead, draw a line which has some data points on each side of the line you are drawing... think of your line as an "average" of the data points.
- Never force a graph to go through the origin (i.e. at x=0 and y=0) unless expressly told to do so.
- Examine your graph: are there one or two points which are farther away from the line than the other points? If so, make sure you plotted them correctly.
- Use regression techniques to find the equation for the best fit for your data. **ALWAYS** include the regression equation with the graph itself.
- Linear regression equations should always be accompanied by the **correlation coefficient**, **r**, and not just R^2. To find r from R^2, take the square root of R^2. If the slope is negative, your r value will be negative as well.

An example graph follows:

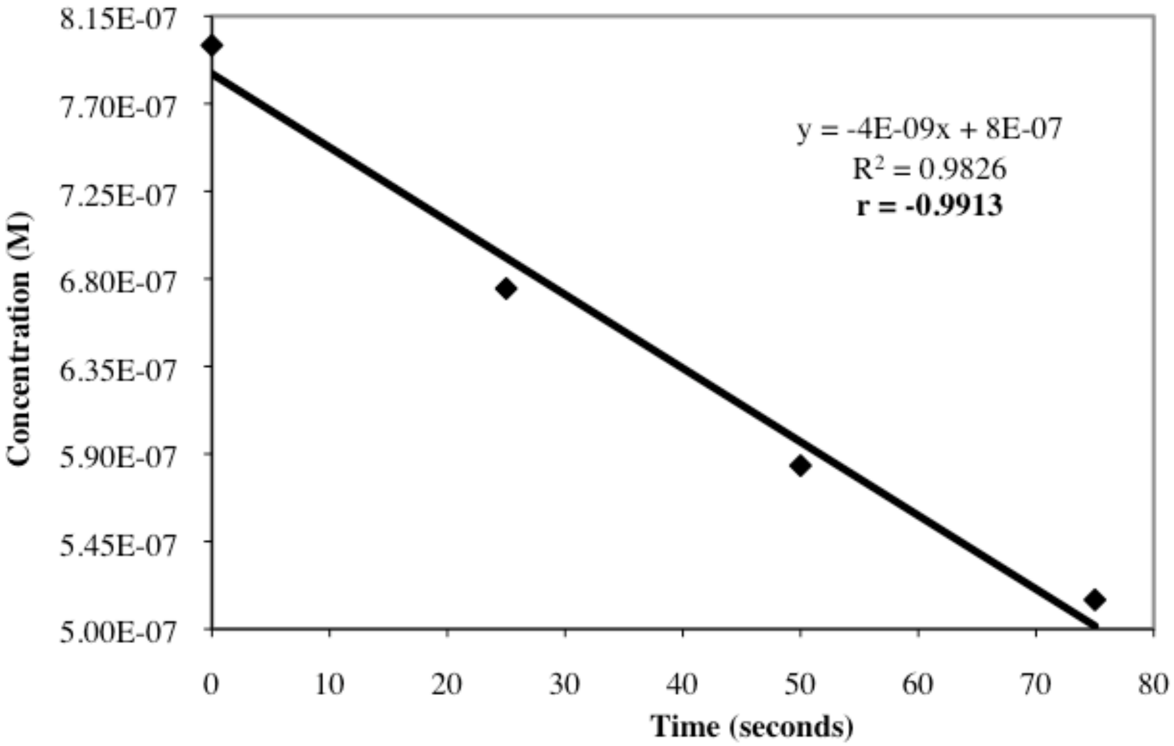
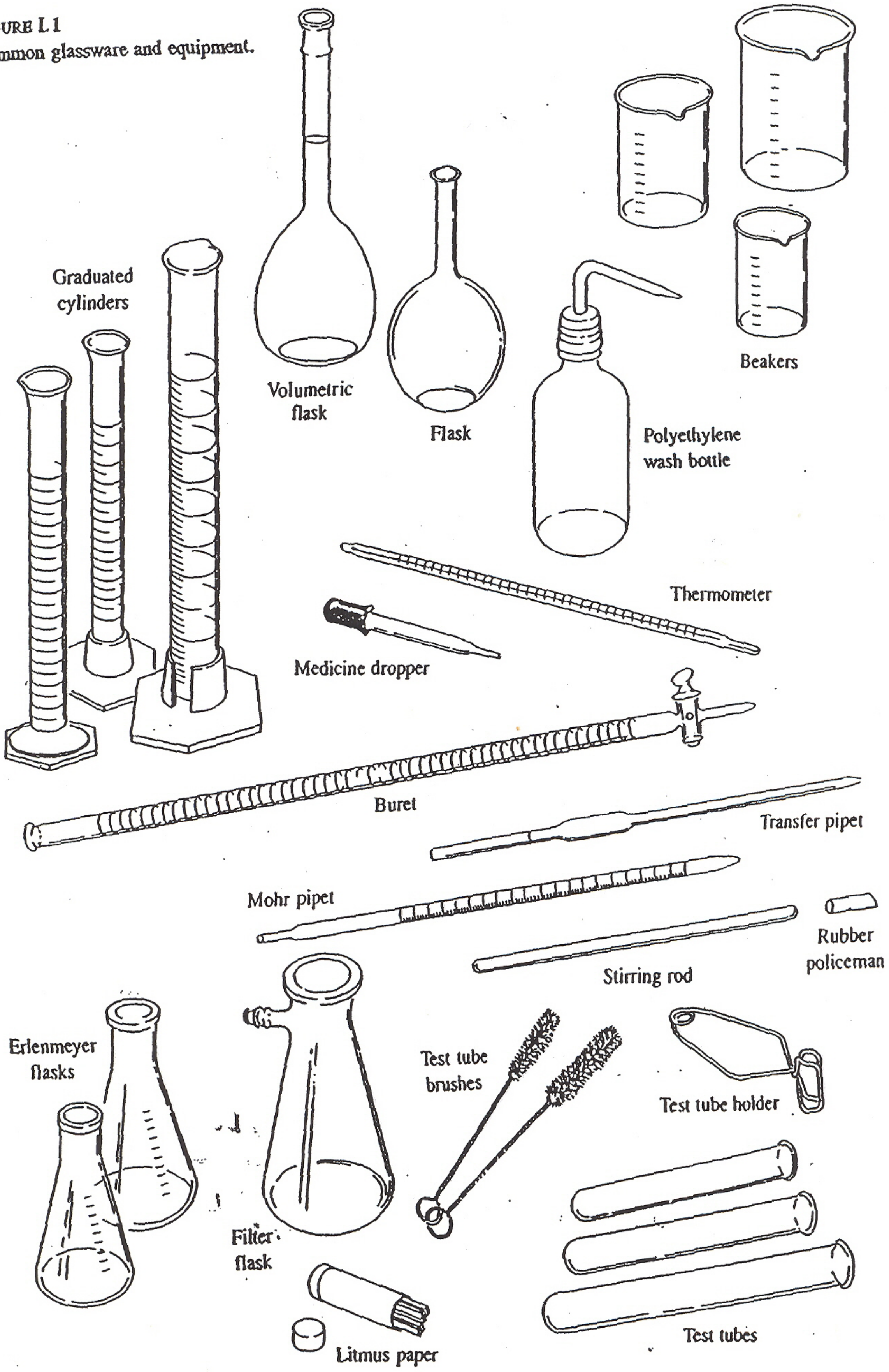
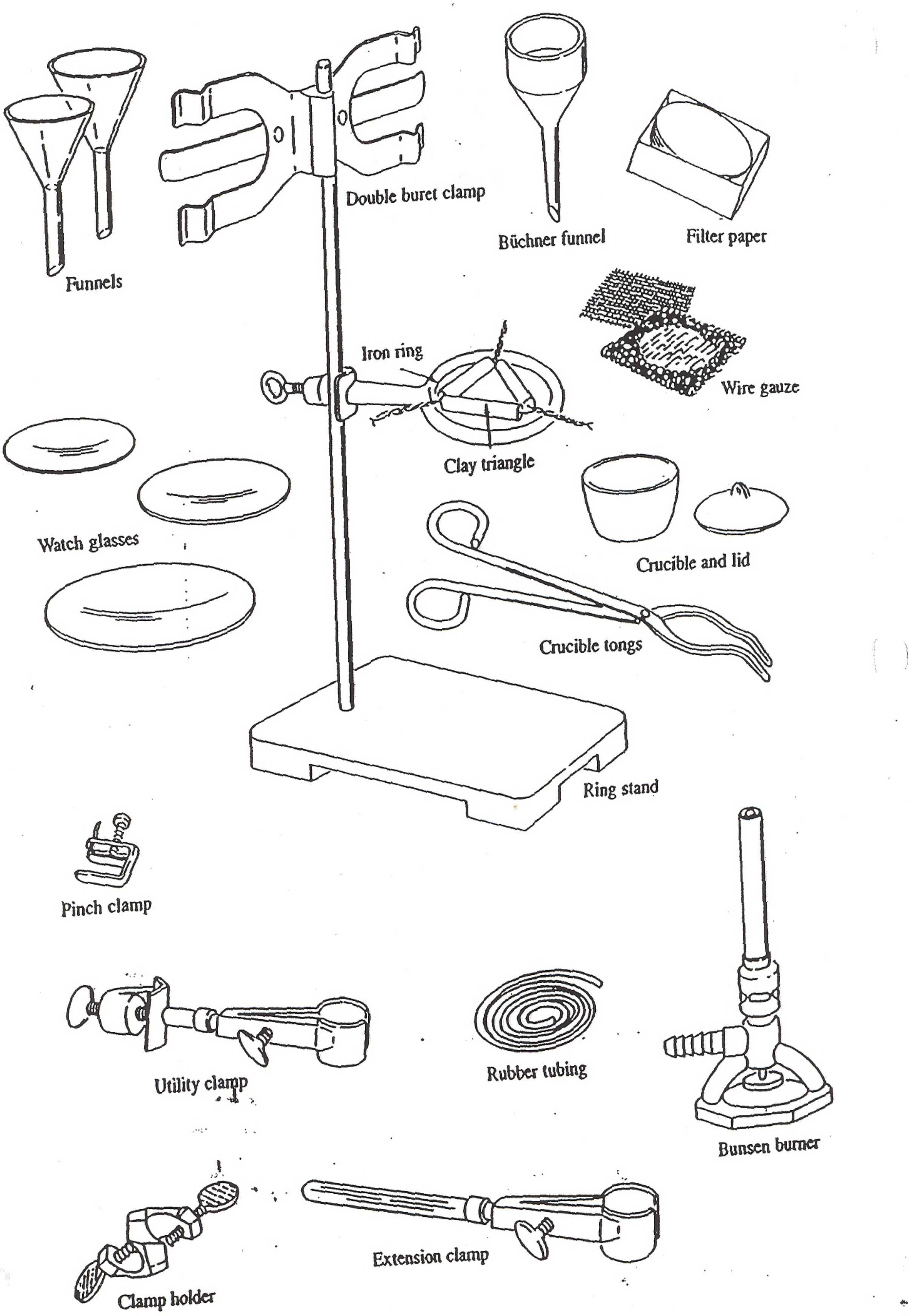

8.15E-07
7.70E-07
7.25E-07
6.80E-07
6.35E-07
5.90E-07
5.45E-07
5.00E-07
Concentration (M)
0
10
20
30
40
50
60
70
80
Time (seconds)
y = -4E-09x + 8E-07
R2 = 0.9826
r = -0.9913

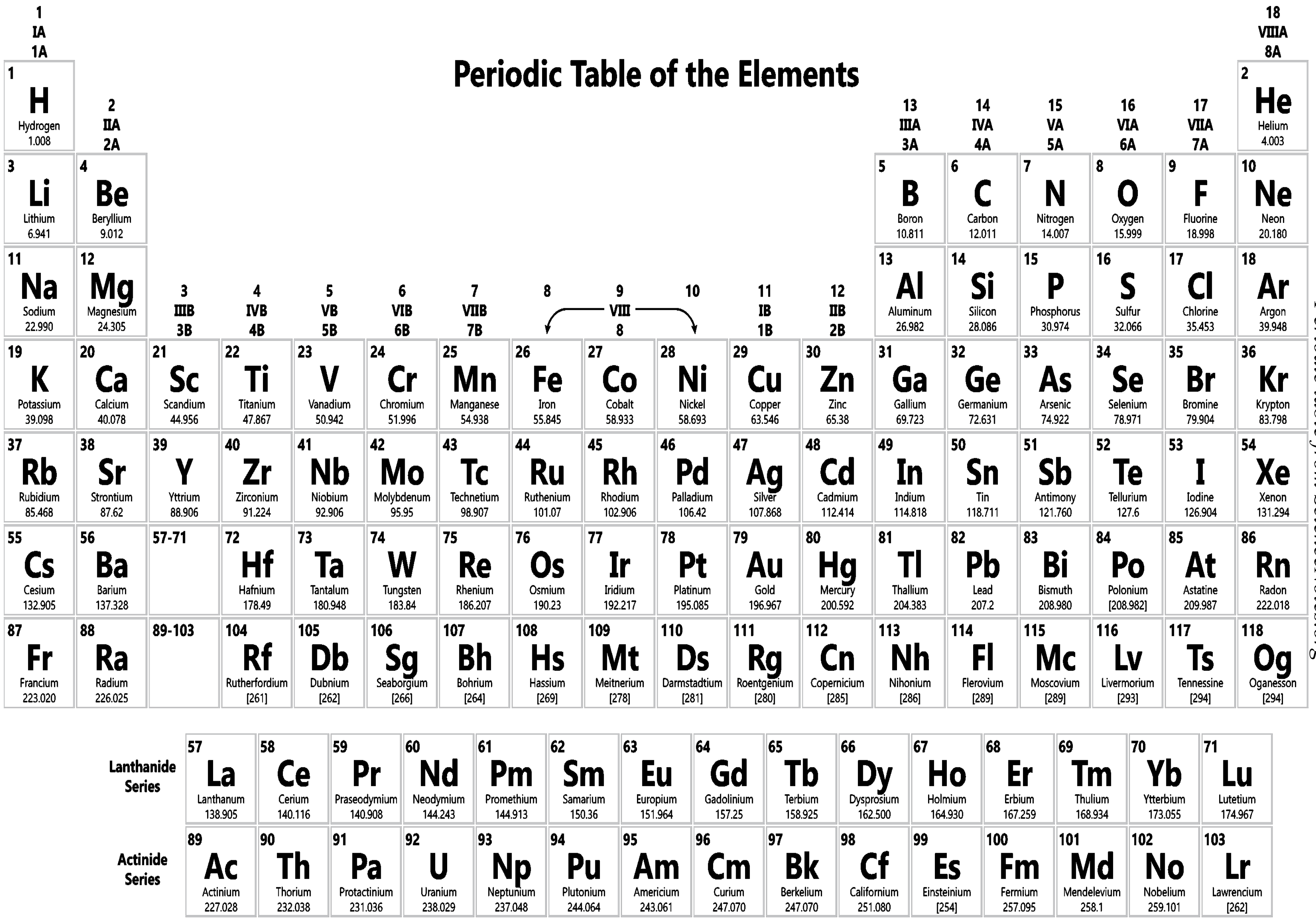
FIGURE I.1
Common glassware and equipment.




Double buret clamp
Büchner funnel
Filter paper
Funnels
Wire gauze
Iron ring
Clay triangle
Watch glasses
Crucible and lid
Crucible tongs
Ring stand
Pinch clamp
Utility clamp
Rubber tubing
Bunsen burner
Extension clamp
Clamp holder

Periodic table from ScienceNotes.org

Periodic Table of the Elements



1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.007	8 **O** Oxygen 15.999	9 **F** Fluorine 18.998	10 **Ne** Neon 20.180
11 **Na** Sodium 22.990	12 **Mg** Magnesium 24.305											13 **Al** Aluminum 26.982	14 **Si** Silicon 28.086	15 **P** Phosphorus 30.974	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.956	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.942	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.938	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.38	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.631	33 **As** Arsenic 74.922	34 **Se** Selenium 78.971	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.798
37 **Rb** Rubidium 85.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.906	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.906	42 **Mo** Molybdenum 95.95	43 **Tc** Technetium 98.907	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.414	49 **In** Indium 114.818	50 **Sn** Tin 118.711	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.6	53 **I** Iodine 126.904	54 **Xe** Xenon 131.294
55 **Cs** Cesium 132.905	56 **Ba** Barium 137.328	57-71	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.085	79 **Au** Gold 196.967	80 **Hg** Mercury 200.592	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium [208.982]	85 **At** Astatine 209.987	86 **Rn** Radon 222.018
87 **Fr** Francium 223.020	88 **Ra** Radium 226.025	89-103	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [278]	110 **Ds** Darmstadtium [281]	111 **Rg** Roentgenium [280]	112 **Cn** Copernicium [285]	113 **Nh** Nihonium [286]	114 **Fl** Flerovium [289]	115 **Mc** Moscovium [289]	116 **Lv** Livermorium [293]	117 **Ts** Tennessine [294]	118 **Og** Oganesson [294]

Lanthanide Series	57 **La** Lanthanum 138.905	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.243	61 **Pm** Promethium 144.913	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.259	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.055	71 **Lu** Lutetium 174.967
Actinide Series	89 **Ac** Actinium 227.028	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium 244.064	95 **Am** Americium 243.061	96 **Cm** Curium 247.070	97 **Bk** Berkelium 247.070	98 **Cf** Californium 251.080	99 **Es** Einsteinium [254]	100 **Fm** Fermium 257.095	101 **Md** Mendelevium 258.1	102 **No** Nobelium 259.101	103 **Lr** Lawrencium [262]

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Parts per Thousand (ppt) Guide

Watch the Parts Per Thousand video here: **http://mhchem.org/pptv**

Parts per thousand (ppt), also known as the “relative standard deviation”, is useful when comparing the uncertainty between different measurements of varying magnitude (i.e. it is a measure of the ***precision*** within an experiment.) **Parts per thousand can be applied to any set of data** where more than one experimental value has been applied – i.e. volumes, percentages, concentrations, etc. We will use parts per thousand often this year, so knowledge of how it works is critical for the successful student.

For the values x_1, x_2 and x_3:

- Take the **average** of the values

$$\text{average} = \frac{\text{sum}}{\#\ \text{of values}} = \frac{x_1 + x_2 + x_3}{3}$$

- Find the **deviation** of each value relative to the average: *deviations will **always** be positive numbers (absolute value)*

$$\textbf{deviation}_1 = \text{absolute value (average} - x_1) = |\,\text{average} - x_1\,|$$
$$\text{deviation}_2 = |\,\text{average} - x_2\,|$$
$$\text{deviation}_3 = |\,\text{average} - x_3\,|$$

- Find the **average deviation** of the deviations

$$\text{average deviation} = \frac{\text{sum of deviations}}{\#\ \text{of values}} = \frac{deviation_1 + deviation_2 + deviation_3}{3}$$

- Calculate the **parts per thousand (ppt)** for the values

$$\textbf{ppt} = \frac{\text{average deviation}}{\text{average}} * 1000$$

<u>*Example*</u>*:* Calculate the parts per thousand for the values 35.72%, 35.92% and 36.02%

- Average = $\frac{35.72 + 35.92 + 36.02}{3}$ = **35.89 %**
- Deviation$_1$ = $|\,35.89 - 35.72\,| = 0.17$
- Deviation$_2$ = $|\,35.89 - 35.92\,| = 0.03$
- Deviation$_3$ = $|\,35.89 - 36.02\,| = 0.13$
- average deviation = $\frac{0.17 + 0.03 + 0.13}{3}$ = **0.11 %**
- parts per thousand = $\frac{0.11}{35.89} * 1000$ = **3.1** *unitless*

Parts per thousand relates the deviation to the magnitude of the experimental data. Consider these two sets of data each with an average deviation of ±0.010:

Data set 1: 0.250 ± 0.010, ppt = (0.010/0.250) x 1000 = 40 ppt (not very good precision).

Data set 2: 4.50 ± 0.010, ppt = (0.010/4.50) x 1000 = 2 ppt (excellent precision)

Although both scenarios have the same deviation, the relative deviation compared to the data gives very different results. Patience and focus is a virtue in this lab.

Spring 2025 Chemistry 223 *with* Dr. Michael A. Russell

For Section 01 and Section H1

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Office: **AC 2568** *Phone:* **(503) 491-7348** *(no texts)*

Email: **mike.russell@mhcc.edu** *or* **mike.russell@mhchem.org**

Office Hours: Held in AC 2568 **MW 10 AM - 11, MW noon - 1 PM** *and* **F 8 AM - 9**
CH 223 Discord Server: **https://discord.gg/fwhD9tf**

Required/Recommended Materials:
- "Chemistry" *by* The OpenStax College (978-1-947172-62-3), *available here for free:* **http://mhchem.org/text/OpenStaxChem.pdf**
- **Chemistry 223 Companion**, *purchase here:* **http://mhcc.edu/bookstore (required)**
- **Scientific calculator** *with at least EXP/EE and ln and log (ideally)* **(required)**
- *iClicker Student App subscription if attending lectures (optional)*

Chemistry 223 website:
http://mhchem.org/223

Course Description: This course offers the fundamental basis of chemistry for science, pre-professional, and chemical engineering majors. A strong emphasis is placed on a mathematical approach. The third term covers equilibrium, introduction to acids and bases, spontaneity of reactions, ionic equilibria, oxidation/reduction and electrochemistry. ***Prerequisites**:* RD090, WR090 and MTH020, each with a grade of "C" or better, or placement above stated course levels; and CH222 with a grade of "C" or better.

Course Philosophy: To be successful, students enrolled in a 200 level chemistry course should complete all assignments before coming to class, attend classes regularly, participate in discussions, and think critically. Homework assignments represent the *minimum* requirement for understanding the principles of chemistry. It is assumed that A and B students will perform enough *unassigned* exercises to master key concepts. I encourage questions in this class, and I expect a considerable amount of work. If you contact me by email, I will respond to you normally within 24 hours; phone messages are discouraged due to the virus.

The Honor Principle: All students will be expected to behave with the highest moral and academic integrity while enrolled in this class. Plagiarism, cheating or sharing information on tests or laboratory reports, disruptive behavior, and other related offenses will be dealt with according to the directives stated in the current *Mt. Hood Community College Student Guide*. Offering, asking for, giving or receiving help from a person or website without instructor consent is cheating. Copying and/or sharing any course materials outside this class is not allowed and illegal due to copyright laws.

Grading:	Midterm Exams (2 total, 140 points each)	280 points	*28% of total*
	Quizzes (6 total, lowest quiz dropped, 20 points each)	100 points	*10%*
	Lecture Final Exam	200 points	*20%*
	Final Lab	80 points	*8%*
	Class Presentation	100 points	*10%*
	Problem sets, worksheets, reserve CP topic	50 points	*5%*
	Nine lab experiments (20 points each)	180 points	*18%*
	Lab Completion Bonus	10 points	*1%*
	Total points:	**1000** points	***100%***

Tentative grading distribution: **A**: 90-100% **B**: 80-89% **C**: 70-79% **D**: 60-69% **F**: less than 60%
Opportunities for extra credit are available and explained in the "Extra-Credit Guide" handout.

Exams and Quizzes will be completed exclusively in class (sections 01 and H1.) Sections 01 and H1 must turn in assignments in person to avoid a point penalty.

Labs and Problem Sets will be submitted on campus (sections 01 and H1.) Sections 01 and H1 must be present during recitation for full credit, and a stamp system will be used to guarantee on-time attendance if necessary.

Each student will submit a **Class Presentation** this term - see the "Class Presentation FAQ" for more information.

Details regarding grading will be discussed during the first week of the term.

"What’s Due This Week" Schedule for CH 223 Spring 2025

All assignments *can be found on our* ***website*** *(http://mhchem.org/223)*

- **Sections 01 and H1** *must bring a printed copy of the lab on the specified day, then turn it in on the deadline during class. Problem sets and labs will be turned in during class in AC 2501; quizzes and exams will be completed during class time. Emailed assignments from Section 01 and H1 students will incur a point penalty, no exceptions.*

Week	Date	Assignment
1	3/31 - 4/4	Introduction *to the course* **01/H1** *Lab:* “Introduce Yourself (in class)” (Lab #1) *due next week in recitation* **01/H1** *Lab:* "Determination of an Equilibrium Constant (in class)“ (Lab #2) *due next week in recitation*
2	4/7 - 4/11	*Due:* Problem set #1 *Chapter 13;* **01, H1:** *due in recitation* *Due:* Quiz #1; **01, H1:** *take in recitation* **01/H1** *Lab:* "Le Chatelier’s Principle (in class)“ (Lab #3) *due next week in recitation* **April 11, 9 AM:** *Last chance to reserve a Class Presentation topic*
3	4/14 - 4/18	*Due:* Problem set #2 *Chapter 14 & 15;* **01, H1:** *due in recitation* *Due:* Quiz #2; **01, H1:** *take in recitation* **01/H1** *Lab:* "Titration Calculations (in class)“ (Lab #4) *due next week in recitation*
4	4/21 - 4/25	*Due:* Problem set #3 *Chapter 14;* **01, H1:** *due in recitation* *Due:* Quiz #3; **01, H1:** *take in recitation* *Due:* **Class Presentation Rough Draft Paper***;* **01, H1**: *due in recitation* **01/H1** *Lab:* "Acid and Base Titrations (in class)“ (Lab #5) *due next week in recitation*
5	4/28 - 5/2	**EXAM #1** - *Chapters 13-15;* **01, H1***: take in recitation* *Due:* "Exam Prep I” *;* **01, H1**: *due in recitation* **01/H1** *Lab:* “Titration of Weak Acids (in class)“ (Lab #6) *due next week in recitation*
6	5/5 - 5/9	**CLASS PRESENTATIONS WEEK** **01/H1:** *Class Presentation paper due at time of presentation during recitation*
7	5/12 - 5/16	*Due:* Problem set #4 *Chapter 15 & 16;* **01, H1:** *due in recitation* *Due:* Quiz #4; **01, H1:** *take in recitation* **01/H1** *Lab:* "Determination of K_{sp}, ΔG°, ΔH° and ΔS° for $Ca(OH)_2$ (in class)” (Lab #7) *due next week in recitation* **May 16:** *Last day to drop or change grade status*

8	5/19 - 5/23	*Due:* Problem set #5 *Chapter 16* & 17*;* **01, H1:** *due in recitation* *Due:* Quiz #5; **01, H1:** *take in recitation* **01/H1** *Lab:* "QA Group I" (Lab #8) *due next week on Wednesday 5/28: Sec 01: 9 AM in AC 1303; Sec H1:1:10 PM in AC 2501*
9	5/26 - 5/30	**Monday, May 26: Memorial Day, all classes, office hours canceled, Sec. 01 schedule changes!** **EXAM #2** *(Chapter 15-17);* **01:** *take on 6/2, 1:10 PM in AC 2501 (Memorial Day)*; **H1***: take on 5/28, 1:10 PM in AC 2501* *Due:* "Exam Prep II" *;* **01:** *due 5/28 at 9 AM in AC 1303;* **H1**: *due 5/28 at 1:10 PM in AC 2501*
10	6/2 - 6/6	*Due:* Problem set #6 *Chapter 18 & 19;* ***All*** *sections self-correct using recitation video.* **01:** *due 6/4 at 9 AM in AC 1303;* **H1:** *due 6/4 at 1:10 PM in AC 2501* **Take Home Quiz #6** *released on website, check email. Sections 01 and H1* ***must*** *print Quiz #6 and turn it in on Wednesday. Quiz 6 due dates:* **01:** *due in lecture on Wednesday, June 4 at 9 AM in AC 1303;* **H1:** *due in recitation on Wednesday, June 4 at 1:10 PM in AC 2501* *Due:* "Final Exam Prep Worksheet"*;* **01:** *due 6/4 at 9 AM in AC 1303;* **H1:** *due 6/4 at 1:10 PM in AC 2501* **01/H1** *Lab:* "QA Group III" (Lab #8) *due same day during lab,* **01:** 6/2 after Exam II (Memorial Day); **H1**: 6/4 at 1:10 PM *(no recitation, meet in AC 2507)* *All extra credit closes Friday, June 6 at 9 AM*
11	6/9 - 6/11	**Take Home Lab Final** *released by 9 AM Monday, 6/9 for all CH 223 sections. Sections 01 and H1* ***must*** *print the Take Home Lab Final and turn it in on Wednesday.* *Section 01: Take* **Lecture Final** *tentatively* on Wednesday, June 11 at 8:45 AM in AC 1303. *Due:* **Take Home Lab Final** *Section H1: Take* **Lecture Final** *tentatively* on Wednesday, June 11 at 1:10 PM in AC 2501. *Due:* **Take Home Lab Final**

Getting Started in Chemistry 223

Welcome to Chemistry 223! I am glad to have you enrolled in CH 223! Here are some hints on how to get started in the class:

- First, **know that I am here to help you succeed in this class**. If you have any questions, please email me (mike.russell@mhcc.edu) or stop by the Discord server (https://discord.gg/fwhD9tf) during office hours. I try to respond to student inquiries within 24 hours.

- There are **two sections of CH 223** this quarter, namely **section 01** (which meets three times a week on campus) and **section H1** (which meets only once a week.) Sections 01 and H1 will have similar schedules. Your experience in this class will depend on which section you are in, so email the instructor (mike.russell@mhcc.edu) if you have any questions about anything, ok?

- **Purchase the Chemistry 223 Companion from the MHCC Bookstore**. The MHCC Bookstore (http://mhcc.edu/bookstore) will ship you a printed copy of this necessary information; alternatively, you can print the document (on our website), but I do not recommend it due to the size of the Companion. You will need access to printed materials this quarter!

- The **"What's Due This Week" Schedule for CH 223** located on page 2 of your syllabus **lists all the problem set due dates, assignment deadlines, labs performed, exam/quiz dates, and related information for this term**. You can plan your term by referencing this handout.... follow it closely and you will do well in CH 223!

- **Check your email often during Chemistry 223**. I will be sending weekly reminders as to “what is due this week” in CH 223 as well as returning some assignments, etc. If you would prefer that I use a non-saints email address to communicate with you, let me know - this is easy to set up!

- The **Chemistry 223 website** is worth exploring. The Chemistry 223 website has a host of learning opportunities waiting for you. You can download and/or print copies of the syllabus, lecture notes, labs, quiz answers, and more; plus there are opportunities for extra credit available. To get started, send your web browser to:

  http://mhchem.org/223

  You should see the CH 223 website on your screen.

- Check out the **Chemistry 223 Chapter Guides** by selecting "**Chapter Guides**" from the upper left hand corner of the CH 223 website. The Chapter Guides offer a detailed approach for studying the course material through a series of online and textbook lessons. **Read Lesson Zero**, the "Intro to the Chapter Guides System," to understand how they work.

- Start thinking about a **Class Presentation Topic**. You will be giving a five-minute presentation this term on a **topic in science that interests you**, and you must reserve your topic choice with me ***BY THE END OF THE SECOND WEEK!*** A written paper also accompanies the presentation on your compound. To reserve your topic, email the instructor, or go here:

  http://mhchem.org/cp223

  The "**Class Presentations FAQ**" (available in the syllabus or here: **http://mhchem.org/cp223info**) has more information.

- The **Chemistry 223 Textbook** is **free** and **legal to download** from our website: http://mhchem.org/text/OpenStaxChem.pdf

- Many opportunities for **extra credit** exist in this class.... see the Extra Credit Guide for more information: **http://mhchem.org/xc**

- You can **download** the entire **Microsoft Office** suite of programs (Word, Excel, PowerPoint, etc.) **for free**… see this link for information: **https://mhcc.edu/OfficeInstall/**

Again, welcome to Chemistry 223! Let me know if I can make your learning experience better in any way, and I look forward to working with you this term! Peace, Dr. Michael Russell (mike.russell@mhcc.edu, 503.491.7348, AC 2568)

CH 223 CLASS PRESENTATIONS FAQ

FAQ = Frequently Asked Questions

When:	**Monday May 5 (section 01) or Wednesday May 7 (section H1)**
What:	A chance to share knowledge with your classmates and the MHCC community
Who:	***Everyone* enrolled in CH 223 (All Sections)**
What topic should I pick?	For CH 223, the topic will be **a topic in science that interests you**. Find a research-quality scientific topic to investigate and complete a report on the topic. All topics ***must*** be approved by Dr. Russell using the online form at **http://mhchem.org/cp223** Once your topic has been approved and reserved, begin researching interesting information on the topic using the library, internet, etc. You will be preparing a paper on your topic and presenting your work to the class in a short (five minute) presentation. If you need to change your class presentation topic after the second week of class for any reason you will be penalized 20 points; hence, it's best to reserve a topic early and start researching promptly. Also, if you still have not reserved a topic by the end of the third week, you will be penalized 20 points for tardiness.
What should I know when writing the paper?	Prepare a paper that is at least **five full pages** of text on your reserved topic. Diagrams, pictures, and other graphics are wonderful, but you will need five full pages of writing for complete credit. The paper should include a separate **cover sheet** with the title of your presentation and your name. The paper must be neat, typed, referenced, and interesting to read; spelling and grammar will count. The paper must use a **"reasonable" font and font size** (Times New Roman, Arial, etc. with size 12 or less); in addition, use **1" margins or less** *(I will measure!)* and **no more than "one and a half" spaced type** (less than double spaced.) If unsure, ask the instructor. A ***separate* page with at least eight references** will be at the end of your paper. References within the paper and at the end should adhere to the "**Class Presentations Citation Guide**" (*found here*: **http://mhchem.org/cg**) For an *example* paper, see: http://mhchem.org/expaper
What is a peer reviewed scientific article?	An important aspect of this assignment is to ensure scientific relevancy. To this end, **find two peer reviewed scientific articles published within the last ten years** that include a reference to your topic. **Include the abstracts of these papers with your final Class Presentation paper.**
How do I find my two peer reviewed scientific articles?	A sure-fire way to access **peer-reviewed scientific articles** is through the MHCC library's article databases. Go here (**https://libguides.mhcc.edu/chemistryguide** - you may have to enter your MyMHCC username and password if you are off campus). Select **Articles (**on the left), then select **ScienceDirect College Edition** (under "Chemistry Databases") or **Academic Search Complete** (under "General Databases"), then search for your topic. ***Remember***, your article citation should include the author(s), year of publication, journal title, title of paper, page number(s), volume of journal, etc. and you will need to include the abstract from the peer reviewed article (but not the entire article!) in your report. Once you conduct a search for your presentation topic, you will likely have a mix of citation/abstract-only and citation/abstract + full-text (whole article) results. You ***only*** need the abstract for your paper - do not include the full article. Here is an **example** of a **peer-reviewed scientific paper with an abstract**: http://mhchem.org/abstr
Tell me about the Class Presentation Rough Draft Paper	During the fourth week, you will be submitting a rough draft of your class presentation paper to the instructor. Ideally this will be the paper in a mostly complete format, but at the very least, two typed pages of text should be submitted. The rough draft should include at least one peer reviewed scientific paper abstract (with its citation) as well as the **Rough Draft Class Presentation form** (http://mhchem.org/rd3) The Class Presentation Rough Draft paper is worth 20 points (out of 100 total.)

What should I know when preparing for the presentation?

You will be creating a five-minute **presentation** on your chosen subject. Sections 01 and H1 will give their presentation during a lab period to their peers. The presentation must be well prepared and interesting; sloppy preparation shows in the presentation portion. Students can use videos, presentation software (PowerPoint, etc.), posters and chalk to enhance their presentation. Presentation software users will be limited to a maximum of six slides; more invokes a penalty.

Please note that using your paper (or a *copy* of your paper) during the presentation will result in a ten point penalty. This will prevent you from "reading" your presentation to the audience.

How will I be graded?

There are 100 points total for this project. 40 points will reflect the work presented in the paper, 40 points will reflect the work done in the presentation and 20 points will be given for completing the Rough Draft Class Presentation paper.

In addition, failure to turn in the "Class Presentation Reviewer Guide" to the instructor at the end of the day of presentations will result in a ten-point penalty. You will be completing the Reviewer Guide while others are giving their presentations. If curious, you can view this guide on our website (http://mhchem.org/cp221info). *This applies to Sections 01 and H1 only.*

Late class presentations will result in a five-point penalty *per day*. The paper and the presentation must be completed for credit on this assignment. Plagiarism discovered from any source will result in a **total** Class Presentation grade of zero.

A sample **Class Presentation Grading Rubric** is available for viewing on the CH 223 website (http://mhchem.org/cgr3). The rubric will allow you to look at the items deemed most important when grading your Class Presentation.

How do I get started?

Step 1: Reserve your Class Presentation Topic

Decide on a scientific topic that interest you, then email the instructor or complete the online web form to reserve your topic: **http://mhchem.org/cp223**

You should receive a response from Dr. Russell within 48 hours after the beginning of the second week of class; if you do not, email him directly at mike.russell@mhcc.edu. Be sure to include alternate topics in case your first choice has already been claimed; he can also pick one for you if you are uncertain which topic to pick. Reserve your class presentation topic by the end of the second week, **April 11** at **9 AM**. You can see which topics are still available here: **http://mhchem.org/223av**

Step 2: Turn in the Class Presentation Rough Draft Paper

The Class Presentation Rough Draft paper should include at least two typed pages and one peer reviewed scientific article and include the handout (http://mhchem.org/rd3) at the beginning of your paper. Deadline: **Mon., April 21 (01)** or **Wed. April 23 (H1)**

Step 3: Give the Class Presentation and turn in your final Class Presentation paper

Section 01 and H1: Bring your final Class Presentation paper and give your presentation during lab. *Section 01:* **Monday, May 5.** *Section H1:* **Wednesday, May 7.**

Before you present and submit your paper, check out the reminders contained within the "**Class Presentation 'Last Minute' Checklist**", found here: http://mhchem.org/cpcs Note that you must both present your work and submit your paper to receive *any* points on this assignment. Also, you cannot "re-use" a Class Presentation topic from CH 221 or CH 222 in CH 223…. these topics must be original for full credit. All presentations over ten minutes in length and all papers with more than 10 pages of writing will suffer a point penalty.

If you have any questions, see this site (http://mhchem.org/cp223info) or contact the instructor.

Name: ________________________________

CH 223 CLASS PRESENTATIONS ROUGH DRAFT PAPER

Staple this form to the ***top*** *of your Rough Draft Class Presentation Paper for full credit*

Lab Section:

Reserved Topic:

Directions:

- This assignment is worth 20 points out of the 100 points assigned to the Class Presentation assignment.
- *Include* at least two typed pages of your Class Presentation report with this form (more is fine!)
- *Include* at least one abstract from a peer reviewed scientific article with a proper citation included (more is fine!)
- This page should be stapled (Sec. 01 and H1) to the **top** of the other pages in this assignment to avoid a five-point penalty

Helpful Resources:

• The CH 223 Class Presentation Frequently Asked Questions handout:	**http://mhchem.org/faq3**
• The CH 223 Citation Guide:	**http://mhchem.org/cg**

Class Presentation Rough Draft Paper Due Dates:

• **Section 01:**	**April 21 at 1:10 PM**
• **Section H1:**	**April 23 at 1:10 PM**

Section 01: *The final Class Presentation paper is due at the time of your presentation on Monday, May 5.*

Section H1: *The final Class Presentation paper is due at the time of your presentation on Wednesday, May 7.*

Staying Connected in Chemistry 223 This Quarter

Success in Chemistry 223 often depends on staying connected with the flow of the course... here are some suggestions on how to be aware of what is happening each week:

- **Discord** is a wonderful medium for keeping students connected while in this class. Our Discord server will offer weekly assignment updates (with links to labs, problem sets, etc.) as well as links to video lectures, tips and hints from the instructor on how to conquer difficult problems, and more! Joining Discord is easy and free; go here (**https://discord.gg/fwhD9tf**) and join the CH 223 server to get started.

- I'd be honored if you would subscribe to me on **YouTube**! (**http://youtube.com/marsmars2**) I create videos for more than just chemistry classes... :)

Additional Syllabus Materials for Chemistry 223 Available on the Internet

Some or all of these materials might prove useful to you in our class. All of them are available on the Chemistry 223 website (https://mhchem.org/223/classroom/ci.htm).

To access these materials (and more!), go to our website (**http://mhchem.org/223)** and select select "**Getting Started**" then "**Other Class Information**" from the upper left corner. Additional materials include:

- The **Extra-Credit Guide** - a helpful guide containing some of the extra credit options available to you in this course

- **Learning Outcomes for CH 223** - a list of "what you will learn" this quarter

- **MHCC College Information** - key information that you, as a student at Mt. Hood Community College, might wish to know, including the **Student Code of Conduct** and **Internet Privacy Policy**

- A **Printable Periodic Table** – this periodic table from ScienceNotes.org will certainly be useful in this course, and you will be able to use this type of periodic table on exams and quizzes.

- The **Chemistry Smiles Generator** – in case you need a smile :) with a chemistry theme.

In addition, the website has a plethora of other "goodies" which may be of assistance to you throughout this quarter... feel free to browse, and if you have questions, please do not hesitate to contact me.

Have a great quarter! Peace,
Michael A. Russell, Ph.D. (he/him/his)
mike.russell@mhcc.edu
(503) 491-7348, AC 2568 (office on campus)
mhchem.org/223

CH 223 Spring 2025: **"Introduce Yourself"** *(in class)* ***Lab:*** *Instructions*

Note: **This is the lab for section 01 and H1 of CH 223 only.**

- *If you are taking section W1 of CH 223*, please use this link: http://mhchem.org/q/1b.htm

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Step One:

Get a printed copy of this lab! You will need a printed (hard copy) version of this lab to turn in on the due date. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.

Step Two:

Complete the next page on your own, then **turn it in at the beginning of recitation to the instructor on Monday, April 7 (section 01)** *or* **Wednesday, April 9 (section H1.)** The graded lab will be returned to you the following week during recitation.

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

Welcome to Chemistry 223! I am glad you enrolled in CH 223 this quarter, and I look forward to an exciting term with you!

On the next page, please describe your post-CH 223 plans in a brief statement. There are no wrong answers as long as you answer the question appropriately.

And remember, you can ask me anything (email is best, mike.russell@mhcc.edu).... to a great term!

Introduce Yourself (in class) Lab - *Worksheet*

YOUR NAME: ____________________________________

Lab Section: ____________________________________

Briefly **describe your post-Chemistry 223 plans in the space below.** (*100 words or less)*

Please note: The instructor will send you email throughout the term, so *please* c*heck your email several times each week!* The instructor will use your @saints.mhcc.edu address by default, but if you wish to use an alternate email address, send an email to mike.russell@mhcc.edu from your alternate email account and it will be changed promptly.

CH 223 Spring 2025: “Determination of an Equilibrium Constant *(in class)*” *Lab - Instructions*

Note: **This is the lab for section 01 and H1 of CH 223 only.**

- *If you are taking section W1 of CH 223*, please use this link:

  http://mhchem.org/q/2b.htm

Step One:

Get a printed copy of this lab! You will need a printed (hard copy) version of pages Ia-2-2 through Ia-2-15 to complete this lab. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.

Step Two:

Bring the printed copy of the lab with you on Monday, March 31 (section 01) *or* **Wednesday, April 2 (section H1.)** During lab in room AC 2507, you will use these sheets (with the valuable instructions!) to gather data, all of which will be recorded in the printed pages below.

Step Three:

Complete the lab work and calculations on your own, then **turn it in** (pages Ia-2-7 through Ia-2-15 *only* to avoid a point penalty) **and your computer generated graph at the beginning of recitation to the instructor on Monday, April 7 (section 01)** *or* **Wednesday, April 9 (section H1.)** The graded lab will be returned to you the following week during recitation.

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

Determination Of An Equilibrium Constant

In this experiment the equilibrium properties of the reaction between the iron(III) ion and the thiocyanate ion will be studied. The relevant chemical equation for this lab is:

$$Fe^{+3}{}_{(aq)} + SCN^{-}{}_{(aq)} \rightleftharpoons FeSCN^{+2}{}_{(aq)} \qquad K_c = \frac{[FeSCN^{+2}]}{[Fe^{+3}][SCN^{-1}]}$$

When solutions of Fe^{+3} and SCN^- are mixed, the above reaction occurs to some extent, forming the *complex ion* $FeSCN^{+2}$. The concentrations of Fe^{+3} and SCN^- will decrease by one mole for every mole of $FeSCN^{+2}$ that forms, but not all of the Fe^{3+} and SCN^- ions will be converted to the complex ion under normal circumstances.

The objective of this experiment is to determine the **equilibrium constant, K_c**, for this reaction. The value of K_c is constant at a given temperature. Any mixture of Fe^{+3} and SCN^- will react until the same value of K_c is obtained. In this experiment, we will determine K_c for this reaction using several different mixtures of Fe^{+3} and SCN^-.

Before we can calculate the value of the equilibrium constant, we must be able to determine the concentration of $FeSCN^{+2}$ in solution. The Beer-Lambert Law, which is commonly referred to as simply **Beer's Law**, relates the absorption of light in a colored sample to its concentration in solution:

$$\mathbf{A = \varepsilon bc = \log (100\% / \%T)}$$

Here **A** is the measured absorbance of the colored solution, ε is the molar absorptivity (with units of M^{-1} cm^{-1}), **b** is the path length (in cm), and **c** is the concentration (molarity, or moles per Liter) of the species being studied, in this case $FeSCN^{+2}$. The value of the molar absorptivity, ε, depends on the solute's overall energy stored within the molecule. $FeSCN^{2+}$ has a deep red color while the reactants are virtually colorless, and only $FeSCN^{2+}$ will absorb light in the visible region.

Absorbance is a unitless quantity that corresponds with the amount of light removed by a colored system. Depending on if you use an analog Spectronic 21 or a digital Vernier SpectroVis, you may need to measure the **percent transmittance (%T)**, or how much light gets through colored solutions. Calculating absorbance from %T is straightforward (A = log (100%/%T).

Because $FeSCN^{+2}$ has a red color, we will use a wavelength appropriate for measuring red light – the SpectroVis will tell us what the exact wavelength will be, but it should be about 450 nm (which is what you'll use when utilizing the Spectronic 21.) Using the Beer's Law equation, we can determine the molar absorptivity constant, ε, for $FeSCN^{+2}$ by measuring its absorbance at different known concentrations of $FeSCN^{2+}$. If absorbance is plotted versus concentration, the *slope* will give the molar absorptivity constant using Beer's Law.

Finding the concentration of $FeSCN^{+2}$ can be achieved using Le Chatelier's Principle. If an excess of Fe^{3+} is added to a small amount of SCN^-, one can assume that the amount of SCN^- present in solution equals the amount of $FeSCN^{2+}$ formed at equilibrium. In other words, we know the final concentration of $FeSCN^{+2}$ in the solution by creating a solution that is not in equilibrium but goes to *completion* using the principle of *limiting reagent*. The SCN^- will be completely converted to $FeSCN^{+2}$, such that the final concentration of $FeSCN^{+2}$ is equal to the initial concentration of SCN^-.

The purpose of this lab is to find the value of the equilibrium constant, K_c. First, you will prepare a series of solutions with known concentrations of $FeSCN^{2+}$ (or SCN^-) and measure the absorbance (or percent transmittance) values at a wavelength appropriate for a red solution around 450 nm. When the absorbance values are plotted versus the concentration of $FeSCN^{2+}$, a linear relationship appears, and ε can be calculated using linear regression (the slope equals εb.). Remember to report the value of the slope, y-intercept and correlation coefficient when using linear regression. ε will allow you to calculate the concentration of $FeSCN^{2+}$ for any combination of Fe^{3+} and SCN^-. You will then prepare a series of solutions with varying amounts of Fe^{3+} and SCN^- initially present, determine the absorbance for $FeSCN^{2+}$, and finally determine the value of K_c at room temperature.

PROCEDURE:

In **Part A**, the goal is to find the molar absorptivity constant, and in **Part B**, you will find the value of the equilibrium constant. Both parts use similar techniques, but **make sure you use the correct reactant concentrations in each section.** Check and double-check the concentrations before analyzing your solutions!

Before you leave lab, it is important that you share data with the other group members (essentially mL of KSCN and absorbance (or %Transmittance) values). Also make sure to get all of the names of your lab partners for your final lab report.

Part A: Determining the Molar Absorptivity Constant (ε)

Place approximately 30 mL of **0.100 M $Fe(NO_3)_3$** in 1 M HNO_3 in a dry labeled 100 mL beaker. The HNO_3 allows the solute components to remain in solution, but it does not affect our calculations in this lab. Note also that there are *two different stock solutions* of $Fe(NO_3)_3$ and KSCN at different concentrations. Make sure you choose the correct solution for part A or your experiment will not work! ***NEVER*** **place solution back into the reagent bottle** - once the solution is removed, the solution has to be placed in the waste bottle.

Place approximately 20 mL of **3.00×10^{-4} M KSCN** into a second dry labeled 100 mL beaker. Clean and dry six 18 x 150 mm test tubes and label 1-5 and B (blank).

Pipet 5.00 mL of the $Fe(NO_3)_3$ solution into tubes 1-5 as demonstrated by the instructor. ***NEVER*** **pipet directly from the bottle, only pipet from a beaker**. Pipet 1, 2, 3, 4, or 5 mL of KSCN into the corresponding labeled test tube. Then add the correct number of mL of water to each test tube so that the *total volume* is 10.00 mL. The sixth test tube is the **blank** (or "dark tube') and will contain only water.

You will need to transfer a small quantity of each solution into a **cuvette** for analysis on your instrument (see below); ideally you will have six cuvettes, one for each of the test tubes from above. Make sure the cuvette is filled to at least 80% of the maximum volume to ensure that light flows through the sample.

You will be using either a Spectronic 21 or a SpectroVis Plus. Follow the appropriate instructions:

Spectronic 21:
Determine the %T for each of the five solutions using a Spec 21 at 450 nm. Assume the path length, b, equals 1.00 cm for these trials. Convert the %T readings into absorbance. Recall that A = log(100%/%T).

SpectroVis Plus:

- Connect the SpectroVis Plus to the LabQuest II. If everything is correct, you should see "USB: Abs" on the screen.
- Place the blank cuvette (with water only) in the SpectroVis, noting the arrow (and direction of light - do not place the "ribbed" walls of the cuvette face the arrow or source of light symbol.)
- Select "Sensors -> Calibrate -> USB: Spectrometer", then press OK if necessary. The following message is displayed: "Waiting 90 seconds for lamp to warm up…" After 90 seconds, the message will change to "Warmup complete" then select "Finish Calibration". When the message "Calibration completed" appears, select OK.
- Place one of the $FeSCN^{2+}$ samples in the SpectroVis. Start data collection by pushing the green "start" button in the lower left corner of the LabQuest 2. A full spectrum graph of the solution will be displayed. Stop data collection (by pressing the red button in the lower left corner) and move the cursor to the maximum wavelength at about 450 nm; this is the wavelength of maximum absorbance (λ max). Record both the wavelength of maximum absorbance and the actual absorbance value in your lab notebook.
- Remove the cuvette and place a new cuvette (with another solution) inside. Repeat the above process until all solutions have recorded values of absorbance and the corresponding λ max (and they should all be about 450 nm.)

You should see a linear relationship between mL of KSCN added and Absorbance; if not, you might want to re-do the measurements. Dispose of the solutions in the waste bottle and clean your beakers and test tubes.

Part B: Determining the Equilibrium Constant (K)

Place approximately 30 mL of **2.00×10^{-3} M $Fe(NO_3)_3$** in 1 M HNO_3 in a dry labeled 100 mL beaker. Place approximately 20 mL of **2.00×10^{-3} M KSCN** in a second dry labeled 100 mL beaker. Clean and dry five 18 x 150 mm test tubes and label 1-5.

Pipet 5.00 mL of the $Fe(NO_3)_3$ solution into tubes 1-5. Pipet 1, 2, 3, 4, or 5 mL of KSCN into the corresponding test tube. Then add the correct number of mL of water to each test tube so that the total volume is 10.00 mL.

Determine the absorbance or %T for each of the five solutions using the Spec 21 (at 450 nm) or the SpectroVis Plus as before. Assume b = 1.00 cm. Convert the %T readings into absorbance values if using the Spec 21 (the SpectroVis does this automatically for you.) You should see a linear relationship between the concentration of KSCN added and Absorbance; if not, you might want to re-do the measurements. Dispose of the solutions in the waste bottle when complete.

Calculations for Part A: *Finding the value of* ε

Determine the diluted molarity of Fe^{+3} and of SCN^- present in each solution using the dilution equation ($M_1 \times V_1 = M_2 \times V_2$).

Example: Find the concentration of SCN^- when 4.00 mL of a $3.00 * 10^{-4}$ M KSCN is diluted to a total of 10.00 mL.

Solution: The initial concentration of KSCN, $3.00 * 10^{-4}$ M, is being diluted to a new solution volume of 10.00 mL. We can use $M_1 \times V_1 = M_2 \times V_2$ equation and solve for M_2.
$M_2 = 3.00 * 10^{-4}$ M * 4.00 mL / 10.00 mL = **$1.20 * 10^{-4}$ M**

Find the concentration of $FeSCN^{2+}$ using the law of limiting reactants.

> *Example:* Find the concentration of $FeSCN^{2+}$ when $[SCN^-] = 1.20 * 10^{-4}$ M and $[Fe^{3+}] = 0.100$ M.
>
> *Solution:* Since $[SCN^-] << [Fe^{3+}]$, it can be assumed that all of the SCN^{-1} has been converted to $FeSCN^{2+}$ using Le Chatelier's Principle. Hence, the $[FeSCN^{2+}]$ at equilibrium equals **$1.20 * 10^{-4}$ M** in this example. *Note:* in part B you will use the value of ε and the absorbance to calculate $[FeSCN^{2+}]$.

Construct a **graph** of absorbance versus the concentration of $FeSCN^{2+}$ on a computer or tablet (no hand drawn graphs.) Perform a **linear regression** on the data, and record your values of the slope, the y-intercept and the correlation coefficient (r). **Determine the value of** ε from the slope (remember that the path length, b, equals 1.00 cm.) **Print this graph** and include it with your final lab report.

Calculations for Part B: *Finding the value of K*

To analyze this set of data, determine the initial molarity of Fe^{+3} and of SCN^- present in each of your five solutions. See the section in Part A for assistance on this procedure.

Calculate the equilibrium concentration of $[FeSCN^{+2}]_{eq}$ in each sample. This can be done using Beer's Law and the molar absorptivity constant determined in part A. $\mathbf{c_{FeSCN} = A / b}\ \varepsilon$

> *Example:* Calculate the equilibrium concentration of $FeSCN^{2+}$ when $\varepsilon = 3420\ cm^{-1}\ M^{-1}$, %T = 45.2%, and b = 1.00 cm.
>
> *Solution:* First convert %T to absorbance. A = log(100%/45.2%) = 0.345
> Now solve for the concentration, c. $c = A / b\ \varepsilon = 0.345 / 1.00\ cm * 3420\ cm^{-1}\ M^{-1}$ = **$1.00 * 10^{-4}$ M**

Next, find the equilibrium concentrations of $[Fe^{+3}]$ and $[SCN^-]$ using the following equations:

$$\mathbf{[Fe^{+3}]_{eq}} = [Fe^{+3}]_{ini} - [FeSCN^{+2}]_{eq} \quad \textit{and} \quad \mathbf{[SCN^-]_{eq}} = [SCN^-]_{ini} - [FeSCN^{+2}]_{eq}$$

where **eq** = equilibrium concentration and **ini** = initial concentration

An **ICE table** may also be helpful (note that $x = [FeSCN^{+2}]_{eq}$):

	$[Fe^{3+}]$	$[SCN^-]$	$[FeSCN^{2+}]$
initial	$[Fe^{3+}]_0$	$[SCN^-]_0$	0
change	- x	- x	+ x
equilibrium	$[Fe^{3+}]_0$ - x	$[SCN^-]_0$ - x	x

Finally, calculate the equilibrium constant, $\mathbf{K_c}$, for each of the five solutions:

$$\mathbf{K_c = [FeSCN^{+2}]_{eq} / \{[Fe^{+3}]_{eq} * [SCN^{-}]_{eq}\}} \quad \textit{or:}$$

$$K_c = \frac{(x)}{\left([Fe^{+3}]_0 - x\right)\left([SCN^{-}]_0 - x\right)}$$

You should have five values of K_c that are all relatively close to each other.

Determine the average K_c value and deviation in parts per thousand (ppt) for your calculations. *See the ppt handout on the CH 223 website or here:* https://mhchem.org/ppt

Determination of an Equilibrium Constant

YOUR NAME: **______________________** ***LAB PARTNER(s):*** **________________**

____

Purpose: To determine the value of an equilibrium constant (K_c) for the following reaction:

$$Fe^{+3}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons FeSCN^{+2}_{(aq)} \qquad K_c = \frac{[FeSCN^{+2}]}{[Fe^{+3}][SCN^{-1}]}$$

Goal #1: **Obtain the Data**

a. **Create the five solutions** as discussed in Part A on page I-2-3**.** Use the Spec-21 *or* SpectroVis to **determine the absorbance (and %Transmittance, if necessary) for each of the five solutions.**

If converting from %T, **Absorbance = log(100%/%Transmittance)** *use base 10 log, not natural log (ln)!*

Data check: The solutions should get progressively more orange/red as the mL of KSCN increase (1.00 mL will be the most dilute, 5.00 mL the most intense.) Also, as mL KSCN increase, the %Transmittance will decrease and the Absorbance increase. If these are not observed, re-create your solutions and try again.

Part A:

mL KSCN	%Transmittance *(if necessary)*	mL KSCN	Absorbance
1.00	______________	1.00	______________
2.00	______________	2.00	______________
3.00	______________	3.00	______________
4.00	______________	4.00	______________
5.00	______________	5.00	______________

Notes: (optional)

Goal #1 (continued)

b. **Create the five solutions** as discussed in Part B on page I-2-4**.** Use the Spec-21 *or* SpectroVis to **determine the absorbance (and %Transmittance, if necessary) for each of the five solutions.**

If converting from %T, **Absorbance = log(100%/%Transmittance)** *use base 10 log, not natural log (ln)!*

Data check: As before, the solutions should get progressively more orange/red as the mL of KSCN increase (1.00 mL will be the most dilute, 5.00 mL the most intense.) Also, as mL KSCN increase, the %Transmittance will decrease and the Absorbance increase. If these are not observed, re-create your solutions and try again.

Part B:

mL KSCN	%Transmittance
1.00	
2.00	
3.00	
4.00	
5.00	

mL KSCN	Absorbance
1.00	
2.00	
3.00	
4.00	
5.00	

Notes: (optional)

Goal #2: **Determine the value of** ε *We will convert the mL of KSCN into a concentration of KSCN. In Part A, the [KSCN] << [Fe^{3+}], so we can assume that [KSCN] = [FeSCN^{2+}]. Next we will convert the %Transmittance values into Absorbance, then make a plot of Absorbance versus [FeSCN^{2+}]. Finally, a linear regression of the Absorbance versus [FeSCN^{2+}] data will lead us to the value of* ε, *the molar absorptivity coefficient, which will be used in the next section.*

a. **Convert mL of KSCN into the diluted concentration of [KSCN] (molarity) using $M_1V_1 = M_2V_2$.** Use **M_1 = 3.00 x 10^{-4} M** for the initial molarity of KSCN and use a final volume V_2 = 10.00 mL. *(see page I-2-4 for an example.)*

b. Since [KSCN] << [Fe^{3+}] in part A, so we can assume that **[KSCN] = [FeSCN^{2+}]**. Write the values for **[FeSCN^{2+}]** in the next column… these will be the x-axis values for your graph. *(see page I-2-4 and 1-2-5 for an example.)*

mL KSCN (V_1)	diluted [KSCN] (M_2)	**[FeSCN^{2+}] (M)**
1.00		
2.00		
3.00		
4.00		
5.00		

Show an example of your work by converting 3.00 mL KSCN into a diluted [KSCN] and then into [FeSCN^{2+}] in the space below.

Goal #2 (continued)

c. Rewrite your Absorbance values ***for Part A*** into the following table (Goal #1, part a) as well as your values for [$FeSCN^{2+}$] (Goal #2, part b).

mL KSCN	Absorbance (Part A)	[$FeSCN^{2+}$] (M)
1.00	____________________	______________
2.00	____________________	______________
3.00	____________________	______________
4.00	____________________	______________
5.00	____________________	______________

d. **Create a computer-generated graph** in a program like Excel, Sheets, Numbers, etc. with **Absorbance versus [$FeSCN^{2+}$]** (Goal #2, part c). **Include the graph with this lab report**. Graphs should be labeled correctly with appropriate axes, and the data should follow a straight line with a positive slope.

Absorbance values are unitless and will constitute the y-axis in the graph. The values for [$FeSCN^{2+}$] will be the x-axis in the graph.

e. **Perform a linear regression of the values used in Goal #2, part d** above (Absorbance versus [$FeSCN^{2+}$]). You can do this in the graphing program you used in Goal #2 part d above, or on your calculator, or using an online linear regression calculator (for example: http://www.alcula.com/calculators/statistics/linear-regression/) The **slope** of the line equals ε, the **molar absorptivity coefficient,** which we will use in Goal #3 next.

The slope should have a value > 1000.

Report the values for slope (ε), y-intercept and the correlation coefficient (r) obtained from the linear regression below:

slope = ε = ___________________________

y-intercept = __________________________

correlation coefficient (r) = ________________________ *(r is not the same as R^2!)*

Make sure you include a computer-generated graph with your lab report!

Goal #3: **Determine the value of K_c.** *We will convert the mL of KSCN and Fe^{3+} into diluted concentrations of KSCN and Fe^{3+} in a method similar to that of Goal #2. We will convert the Part B %Transmittance values into absorbance, then we can use our* **ε**, the **molar absorptivity coefficient**, *to calculate the equilibrium concentrations of $FeSCN^{2+}$ using the Beer-Lambert Law. Finally, using ICE tables, we will calculate the equilibrium concentrations of Fe^{3+}, SCN^{-1} and $FeSCN^{2+}$ in order to calculate K_c, the equilibrium constant for this lab.*

a. **Convert mL of KSCN into the diluted concentration of [KSCN] (molarity) using $M_1V_1 = M_2V_2$.** Use **$M_1 = 2.00 \times 10^{-3}$ M** for the initial molarity of KSCN and use a final volume $V_2 = 10.00$ mL. *(see page I-2-4 and Goal #2 section a for examples.)*

b. **Convert mL of Fe^{3+} into the diluted concentration of $[Fe^{3+}]$ (molarity) using $M_1V_1 = M_2V_2$.** Use **$M_1 = 2.00 \times 10^{-3}$ M** for the initial molarity of Fe^{3+} and use a final volume $V_2 = 10.00$ mL. *These calculated M_2 values should all be the same since the initial volume (V_1) are identical! (see page I-2-4 and Goal #2 section a for examples.)*

mL KSCN (V_1)	**diluted [KSCN] (M_2)**	**mL Fe^{3+} (V_1)**	**diluted $[Fe^{3+}]$ (M_2)**
1.00		5.00	
2.00		5.00	
3.00		5.00	
4.00		5.00	
5.00		5.00	

Note:

- We will refer to "diluted [KSCN]" values as **$[SCN^{-1}]_i$ in Goal #3, part e, below**
- We will refer to "diluted [**Fe^{3+}**]" values as **$[Fe^{3+}]_i$ in Goal #3, part f, below**

Show an example of your work by showing how to convert 3.00 mL KSCN into a diluted [KSCN]:

Show an example of your work by showing how to convert 5.00 mL Fe^{3+} into a diluted $[Fe^{3+}]$:

Goal #3 (continued)

c. Rewrite your Absorbance (and %Transmittance values, if used) **for Part B** into the following table (Goal #1, part b).

Absorbance values are unitless and will constitute the y-axis in the graph.

mL KSCN	%Transmittance (*if used*)	Absorbance (Part B)
1.00		
2.00		
3.00		
4.00		
5.00		

d. Using Beer-Lambert Law, we can convert your Absorbance (A) values (Goal #3, part c) into **concentration of $[FeSCN^{2+}]$** using:

$$\textbf{Absorbance} = A = \varepsilon bc$$

In this equation, **A** = Absorbance (Goal #3, part c), ε = the molar absorptivity coefficient (from Goal #2, part e), **b** = path length (for this lab, b = 1.00 cm) and **c =** concentration of $[FeSCN^{2+}]$ (in mol/L, or just M). You want to solve for the **equilibrium concentration of $[FeSCN^{2+}]$**, so **c = A/εb**

value of ε = ____________________ *(from Goal #2, part e)*

mL KSCN	**Absorbance**	**$[FeSCN^{2+}]_{eq}$ (M)**
1.00		
2.00		
3.00		
4.00		
5.00		

Goal #3 (continued)

e. We can use the values of **$[FeSCN^{2+}]_{eq}$** from Goal #3, part d (above) to find the equilibrium values of $[SCN^{-1}]$ or $[SCN^{-1}]_{eq}$. To find the equilibrium values of $[SCN^{-1}]_{eq}$ do the following:

$$[SCN^{-1}]_{eq} = [SCN^{-1}]_i - [FeSCN^{2+}]_{eq}$$

- **$[SCN^{-1}]_i$** values can be found in Goal #3, part b above
- **$[FeSCN^{2+}]_{eq}$** values can be found in Goal #3, part d above

mL KSCN	**$[SCN^{-1}]_i$**	**$[FeSCN^{2+}]_{eq}$**	**$[SCN^{-1}]_{eq}$**
1.00			
2.00			
3.00			
4.00			
5.00			

f. In a similar fashion, we can use the values of $[FeSCN^{2+}]_{eq}$ from Goal #3, part d to find the equilibrium values of $[Fe^{3+}]$ or $[Fe^{3+}]_{eq}$. To find the equilibrium values of $[Fe^{3+}]_{eq}$ do the following:

$$[Fe^{3+}]_{eq} = [Fe^{3+}]_i - [FeSCN^{2+}]_{eq}$$

- **$[Fe^{3+}]_i$** values can be found in Goal #3, part b above - *they should be all identical!*
- **$[FeSCN^{2+}]_{eq}$** values can be found in Goal #3, part d above

mL Fe^{3+}	**$[Fe^{3+}]_i$**	**$[FeSCN^{2+}]_{eq}$**	**$[Fe^{3+}]_{eq}$ (M)**
5.00			
5.00			
5.00			
5.00			
5.00			

Goal #3 (continued)

g. We can use the equilibrium values of $[Fe^{3+}]_{eq}$, $[SCN^{-1}]_{eq}$ and $[FeSCN^{2+}]_{eq}$ to calculate the value of $\mathbf{K_c}$**.**

$$\mathbf{K}_c = \frac{\mathbf{[FeSCN^{+2}]}}{\mathbf{[Fe^{+3}][SCN^{-1}]}}$$

- $\mathbf{[FeSCN^{2+}]_{eq}}$ values can be found in Goal #3, part d above
- $\mathbf{[SCN^{-1}]_{eq}}$ values can be found in Goal #3, part e above
- $\mathbf{[Fe^{3+}]_{eq}}$ values can be found in Goal #3, part f above

$\mathbf{[FeSCN^{2+}]_{eq}}$	$\mathbf{[SCN^{-1}]_{eq}}$	$\mathbf{[Fe^{3+}]_{eq}}$	$\mathbf{K_c}$

Average of five $\mathbf{K_c}$ values = ____________________

Parts per thousand = _________________________

Info on parts per thousand: **https://mhchem.org/ppt**

In the space below, show *how* you calculated the first K_c value, the average of the five K_c values, and the parts per thousand.

Postlab Questions:

A student mixes 5.00 mL of 2.00 x 10^{-3} M $Fe(NO_3)_3$ with 5.00 mL 2.00 x 10^{-3} M KSCN. She finds that in the equilibrium mixture the concentration of $FeSCN^{+2}$ is 1.40 x 10^{-4} M. $\mathbf{Fe^{+3}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons FeSCN^{+2}_{(aq)}}$

a. What is the initial concentration in solution of the Fe^{+3} and SCN^{-}?

b. Create an ICE table for this problem. What is the equilibrium constant value for this reaction?

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CH 223 Spring 2025:
“Le Chatelier's Principle *(in class)”* ***Lab*** *- Instructions*

Note: **This is the lab for section 01 and H1 of CH 223 only.**

- *If you are taking section W1 of CH 223*, please use this link:
  http://mhchem.org/q/3b.htm

Step One:

Get a printed copy of this lab! You will need a printed (hard copy) version of pages Ia-3-2 through Ia-3-12 to complete this lab. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.

Step Two:

Bring the printed copy of the lab with you on Monday, April 7 (section 01) *or* **Wednesday, April 9 (section H1.)** During lab in room AC 2507, you will use these sheets (with the valuable instructions!) to gather data, all of which will be recorded in the printed pages below.

Step Three:

Complete the lab work and calculations on your own, then **turn it in** (pages Ia-3-7 through Ia-3-12 *only* to avoid a point penalty) **at the beginning of recitation to the instructor on Monday, April 14 (section 01)** *or* **Wednesday, April 16 (section H1.)** The graded lab will be returned to you the following week during recitation.

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

Le Chatelier's Principle

Chemical systems tend to exist in a state of equilibrium. If this equilibrium is disturbed, the reaction may shift in the forward or reverse direction. If the principles governing the equilibrium system are understood, then predictions can be made as to how to drive the reaction in the forward or reverse directions.

In the following equilibrium system, in which A, B, and C are molecules or ions in solution, their relative concentrations at a given temperature must equal a constant, **K**:

$$\mathbf{a\,A(aq) \rightleftharpoons b\,B(aq) + c\,C(aq)} \qquad \text{equilibrium constant} = K = \frac{[B]^{b}[C]^{c}}{[A]^{a}}$$

For K to remain constant, if any concentrations are altered, the other components must also shift in concentration. For example, if the concentration of A is increased, the concentrations of B and C will also increase to keep K at a constant value. The reaction shifts in the forward direction. If the concentration of B or C is increased, the reaction will shift in the reverse direction thereby increasing the concentration of A and lowering the concentrations of both B and C. Furthermore, if the concentration of A is reduced, the reaction will shift in the reverse direction, lowering the concentrations of B and C and subsequently increasing the concentration of A to balance the equilibrium. *If you attempt to change a system in chemical equilibrium, it will react in such a way to counterbalance the change you attempted.*

In addition to changes in concentration, a change in the temperature of the system will affect the equilibrium. If the reaction is exothermic in the forward direction, such that heat is a product, an increase in temperature will shift the reaction in the reverse direction. Therefore, an increase in temperature favors the endothermic reaction.

In solution, there are often more than one equilibria maintained. The most important equilibrium involves the dissociation of water:

$$\mathbf{H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)}$$

This equation must always be in equilibrium in aqueous solution. If H^+ ion or OH^- ion are present in another equilibrium solution, the equilibrium can be affected by adding acid or base to the system (parts A and D in the procedure). However, if neither H^+ ion nor OH^- ion is present in the equilibrium equation, the equilibrium will not be influenced by the addition of acids or bases (parts B and C).

PROCEDURE:

In this experiment you will work with several equilibrium systems, varying conditions such as temperature and concentrations thereby forcing shifts in the forward or reverse directions. You will be asked to interpret your observations in terms of the principles presented above.

The waste from parts B and C should be poured in a waste bottle. Parts A and D may be poured down the drain.

PROCEDURE: Part A: Solubility Equilibrium: Finding a value for K_{sp}

Many ionic compounds have limited water solubility, dissolving only partially in water. An example is $PbCl_2$:

$$\mathbf{PbCl_2(s) \rightleftharpoons Pb^{+2}(aq) + 2\ Cl^{-}(aq) \quad K_{sp} = [Pb^{+2}][Cl^{-}]^2}$$

The concentration of $PbCl_2$ does not enter into the equilibrium equation because it is a solid and therefore has a constant effect on the system, independent of its amount. The equilibrium constant for a solubility equilibrium is called the **solubility product constant** and symbolized as $\mathbf{K_{sp}}$. For this equilibrium to exist, there must be some solid $PbCl_2$ present in the system. If there is no solid present, there is no equilibrium.

1. Set up a hot water bath using a 400 mL beaker for step 2 below. To a (room temperature) test tube, add 5.0 mL 0.30 M $Pb(NO_3)_2$. Add 0.30 M HCl in 0.5 mL increments (10 drops) to the $Pb(NO_3)_2$ until a white precipitate forms.
   a. Record the volume of HCl needed and determine the moles of Cl^- present in your solution.
   b. Determine the moles of Pb^{+2} ion present in the final solution.
   c. Calculate K_{sp}. (Note: You must use *diluted* concentrations of ions in mol/L)
   d. Why did the $PbCl_2$ not precipitate immediately on addition of HCl?
2. Observing the effect of temperature on the system can determine the sign of enthalpy for this reaction.
   a. Place the test tube in hot water and record your observations.
   b. Place the test tube in cold water and record your observations.
   c. What is the sign of ΔH for the above reaction? Explain.
   d. What happened to the value of K_{sp} in the hot solution? (Increase, decrease, no change) Explain.
3. Add deionized water to the test tube in 0.5 mL increments, stirring well after each addition.
   a. Record the volume of water added when the precipitate just dissolves.
   b. Calculate the molar concentration of Pb^{+2} and Cl^{-1} ions and your reactant quotient (Q).
   c. Explain why the $PbCl_2$ dissolved in water.

Part B: Complex Ion Equilibria

Many metallic ions exist as **complex ions** in solution, combining with other ions or molecules called **ligands**. While complex ions are stable, they may be converted to other complex ions by the addition of ligands that form more stable complexes. Common ligands include OH^-, NH_3, and Cl^-, etc. In this section the cobalt (II) ion can exist as either the **pink** complex ion $Co(H_2O)_6^{+2}(aq)$ or the **blue** complex ion $CoCl_4^{-2}(aq)$ depending on the conditions. The principles of equilibrium can be used to predict which ion will be present.

$$\mathbf{Co(H_2O)_6^{+2}(aq,\ pink) + 4\ Cl^{-}(aq) \rightleftharpoons CoCl_4^{-2}(aq,\ blue) + 6\ H_2O(l)}$$

1. Place a few crystals of $CoCl_2$ - 6 H_2O in a regular test tube. Record the color and determine the Co(II) complex ion present in solution for each of the following. Explain.

a. Add 2 mL (40 drops) of 12 M HCl (CAUTION) and stir to dissolve the crystals.
b. Add 2 mL increments of deionized H_2O to the test tube until no further color change occurs.
c. Place the sample in hot water and cold water and record the color change. What is the sign of ΔH for the above equation? Explain.

Part C: Acid-Base Indicators

Acid-base indicators are chemical substances which change color in solution when [H^+] changes. Methyl violet (HMV) is an example of an acid-base indicator. In solution, HMV dissociates as follows:

$$\textbf{HMV(aq, yellow)} \rightleftharpoons \textbf{H}^+\textbf{(aq)} + \textbf{MV}^-\textbf{(aq, violet)}$$

In solution, HMV has an intense yellow color while MV^- is violet. Therefore, a change in [H^+] will affect the color of the indicator solution.

1. Add 5 mL of deionized H_2O to a test tube. Add a few drops of methyl violet indicator. Record the color.
2. What reagent could be added to shift the equilibrium (change color)? Design and test your hypothesis to demonstrate this equilibrium shift. Explain your results.
3. What reagent could be added to shift the equilibrium back to its original color? Design and test this hypothesis. Explain your results.

Part D: Dissolving Insoluble Solids

Not all solids will dissolve by adding more water or heating the solution. However, in these cases we can employ the principles of equilibrium to dissolve solids. We will use $Zn(OH)_2$ as an example:

$$\mathbf{Zn(OH)_2(s) \rightleftharpoons Zn^{+2}(aq) + 2\,OH^-(aq)} \textit{ where } \mathbf{K_{sp} = [Zn^{+2}][OH^-]^2 = 5 \times 10^{-17}}$$

The equilibrium constant for this dissociation is quite small, indicating that the reaction does not go very far to the right. Thus, $Zn(OH)_2$ is virtually insoluble in water. In a saturated solution, [Zn^{+2}] x [OH^-]^2 must equal 5 x 10^{-17}. However, if this product is somehow lowered to less than 5 x 10^{-17}, then $Zn(OH)_2$ will dissolve until the products equal K_{sp}, where equilibrium will again be obtained. To do this, the concentration of one of the products must be lowered rather drastically. Using a second equilibrium present in solution:

$$\mathbf{H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)}$$

the addition of an acid to the solution will increase [H^+] and thereby lower [OH^-]. This in turn will drive the above reaction to the right, dissolving $Zn(OH)_2$.

Alternatively, we can lower the concentration of Zn^{+2} ion by taking advantage of the fact that zinc ion forms stable **complex ions** with OH^- and NH_3:

$$\mathbf{Zn^{+2}(aq) + 4\,OH^-(aq) \rightleftharpoons Zn(OH)_4^{-2}(aq) \qquad K_1 = 3 \times 10^{15}}$$
$$\mathbf{Zn^{+2}(aq) + 4\,NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{+2}(aq) \qquad K_2 = 1 \times 10^{9}}$$

In high concentrations of OH^- or NH_3, the above reactions are driven to the right, lowering [Zn^{+2}].

1. To each of three small test tubes, add about 2 mL 0.1 M $Zn(NO_3)_2$. Add one drop 6M NaOH to each test tube and stir. Record your observations.

   a. To the first test tube add 6 M HCl drop by drop. Record and explain your observations.
   b. To the second test tube add 6 M NaOH drop by drop. Stir well and explain your observations.
   c. To the third test tube add 6 M NH_3 (or NH_4OH) drop by drop. Stir well and explain your observations.

2. Repeat the above procedure using 2 mL of 0.1 M $Mg(NO_3)_2$ instead of $Zn(NO_3)_2$ in three separate test tubes. Add one drop of 6 M NaOH to each test tube and stir. Record your observations.
   a. Use the same volume of HCl as you used with the $Zn(NO_3)_2$, above, and stir well. Record your observations.
   b. Use the same volume of 6 M NaOH as you used with the $Zn(NO_3)_2$, above, and stir well. Record your observations.
   c. Use the same volume of 6 M NH_3 (or NH_4OH) as you used with the $Zn(NO_3)_2$, above, and stir well. Record your observations.

3. Explain the following in your report:
   a. What insoluble hydroxide formed when one drop of NaOH was added to the $Zn(NO_3)_2$? To the $Mg(NO_3)_2$?
   b. Explain why some of the reactions were similar between the two metal ions and why some were different.
   c. Why does an insoluble hydroxide tend to dissolve in acidic solution?
   d. Does Mg^{+2} ion appear to form complex ions with OH^- and NH_3? Explain.

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Le Chatelier's Principle

YOUR NAME: ______________________ ***LAB PARTNER(s):*** ________________

Purpose: To explore Le Chatelier's Principle through four different chemical scenarios. Follow the instructions and learn about Le Chatelier's Principle!

***Goal** #1:* **Part A: Solubility Equilibrium: Finding a value for K_{sp}**

1. Set up a hot water bath using a 400 mL beaker for step 2 below. To a (room temperature) test tube, add **5.0 mL 0.30 M $Pb(NO_3)_2$.** Add **0.30 M HCl in 0.5 mL increments (10 drops)** to the $Pb(NO_3)_2$ until a white precipitate forms.

Write the **Ksp chemical equation** used in this section:

How many mL of $Pb(NO_3)_2$ were used? _________________ mL

How many mL of HCl did you use? _________________ mL

Total volume of $Pb(NO_3)_2$ and HCl = _________ mL *(add up two previous volumes)*

Calculate the moles of Pb^{2+} added to the solution: __________________ moles

Calculate the moles of Cl^{-1} added to the solution: __________________ moles

Calculate the concentration (M) of Pb^{2+} at equilibrium: __________________ M (*use total volume!)*

Calculate the concentration (M) of Cl^{-1} at equilibrium: __________________ M (*use total volume!)*

Calculate the value of $K_{sp} = [Pb^{2+}][Cl^{-1}]^2$ K_{sp} = ________________________

Remember: $[Pb^{2+}] = Pb(NO_3)_2$ *(M)* and $[Cl^{-1}] = HCl$ *(M)*. **Show work!**

Goal #1: **Part A** *continued*

2. Observing the effect of temperature on the system can determine the sign of enthalpy for this reaction.

* Place the test tube in hot water and record your observations. What happened to the solid $PbCl_2$ as it was heated up?

* Place the test tube in cold water and record your observations. What happened to the $PbCl_2$ solution as it was cooled down?

* Remembering that K_{sp} is defined here as: $\mathbf{PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^{-1}(aq)}$, is this reaction **endothermic** or **exothermic**? Explain.

3. Add deionized water to the test tube in 0.5 mL increments, stirring well after each addition

How much water did you add to the solution to make the $PbCl_2(s)$ disappear? _________ mL

Calculate the value of $Q = [Pb^{2+}][Cl^{-1}]^2$ Q = ________________________ **Show work!**

Hint: use moles of $Pb(NO_3)_2$ and HCl from the previous page, divide each by the total volume (which includes the water added in the previous question) to find $[Pb^{2+}]$ and $[Cl^{-1}]$, then calculate Q.

Goal #2: Part B: Complex Ion Equilibria

Place a few crystals of $CoCl_2$ - 6 H_2O in a regular test tube. Record the color and determine the Co(II) complex ion ("pink" or "blue" will be fine) present in solution for each of the following.

Write the **chemical equation** used in this section:

* Add 2 mL (40 drops) of 12 M HCl (CAUTION) and stir to dissolve the crystals.

When HCl was added to the crystals, what color was observed? (circle one) **Pink** **Blue**

* Add 2 mL increments of deionized H_2O to the test tube until no further color change occurs.

When water was added to the solution, what color was observed? (circle one) **Pink** **Blue**

* Place the sample in hot water and cold water and record the color change.

Explain what happened when the sample was added to hot water and cold water:

Is this reaction **endothermic** *(positive ΔH)* or **exothermic** *(negative ΔH)*? Explain.

Goal #3: Part C: Acid-Base Indicators

1. Write the **chemical equation** used in this section:

2. Add 5 mL of deionized H_2O to a test tube. Add a few drops of methyl violet indicator.

When drops of methyl violet are added to water, what color is observed? **Yellow** **Violet**
(circle one)

What chemical (reagent) can be used to change the color of the solution? Add the chemical and state what chemical you used (include the concentration.) (*hint:* this is an *acid-base* indicator.)

What chemical (reagent) can be used to change the color of the solution back to the original color? Add the chemical to observe the change; state what chemical you used (include the concentration.) Explain why adding this reagent worked.

Goal #4: **Part D: Dissolving Insoluble Solids - the Zinc Test**

1. To each of three small test tubes, add about 2 mL 0.1 M $Zn(NO_3)_2$. Add one drop 6M NaOH to each test tube and stir.

> When one drop of NaOH was added to each of the three Zn-containing test tubes, what was observed? Explain why this happened and **identity** the white solid.

* To the first test tube add 6 M HCl drop by drop. Record and explain your observations.

> Explain what happened when HCl was added to the first white solid-containing test tube. Do acids appear to dissolve insoluble hydroxides?

* To the second test tube add 6 M NaOH drop by drop. Stir well and explain your observations.

> Explain what happens when excess NaOH is added to the second white solid-containing test tube. Do you think that the complex ion ($\mathbf{Zn(OH)_4^{-2}(aq)}$) could have formed? Explain.

* To the third test tube add 6 M NH_3 (or NH_4OH) drop by drop. Stir well and explain your observations.

> Explain what happens when NH_3 is added to the third white solid-containing test tube. Do you think that the complex ion ($\mathbf{Zn(NH_3)_4^{+2}(aq)}$) could have formed? Explain.

***Goal** #4:* **Part D: Dissolving Insoluble Solids - the Magnesium Test**

2. Repeat the above procedure using 2 mL of 0.1 M $Mg(NO_3)_2$ instead of $Zn(NO_3)_2$ in three separate test tubes. Add one drop of 6 M NaOH to each test tube and stir.

When one drop of NaOH is added to each of the three Mg-containing test tubes, what is observed? Explain why this happened and **identity** the white solid.

* Use the same volume of HCl as you used with the $Zn(NO_3)_2$, above, and stir well. Record your observations.

Explain what happened when HCl was added to the first white solid-containing test tube. Do acids appear to dissolve insoluble hydroxides?

* Use the same volume of 6 M NaOH as you used with the $Zn(NO_3)_2$, above, and stir well. Record your observations.

Explain what happened when excess NaOH was added to the second white solid-containing test tube. Do you think that a complex ion could have formed? Explain.

* Use the same volume of 6 M NH_3 (or NH_4OH) as you used with the $Zn(NO_3)_2$, above, and stir well. Record your observations.

Explain what happened when NH_3 was added to the third white solid-containing test tube. Do you think that a complex ion could have formed? Explain.

In terms of electron orbitals, what differences can be found between zinc and magnesium?

Do complex ions appear to form easier with main group metals or transition metals? Why?

Postlab Questions:

1. Methyl orange (HMO) is a common acid-base indicator. In solution it ionizes according to the equation:

   HMO(aq, red) $\rightleftharpoons$ H^+(aq) + MO^- (aq, yellow)

   Chat adds 5 mL of deionized water to a test tube and adds 5 drops of methyl orange. He is captivated by the lovely yellow color of the solution.

   a. If Chat adds 6 M HCl to his solution, what color will he observe? Explain.

   b. If Chat next adds 6 M NaOH to the solution, what color will be observed? Explain.

2. Zinc hydroxide is relatively insoluble in water. The reaction is represented as:

   $Zn(OH)_2$(s) $\rightleftharpoons$ Zn^{+2}(aq) + 2 OH^-(aq)

   a. What is the equilibrium expression for the above reaction?

   b. For $Zn(OH)_2$ to be soluble in solution, [Zn^{+2}] or [OH^-] must be relatively small. Explain.

   c. Would you expect $Zn(OH)_2$ to dissolve if acid were added to the solution? Explain.

CH 223 Spring 2025:
“Titration Calculations *(in class)”* ***Lab*** *- Instructions*

Note: **This is the lab for section 01 and H1 of CH 223 only.**

- *If you are taking section W1 of CH 223*, please use this link: http://mhchem.org/q/4b.htm

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Step One:

Get a printed copy of this lab! You will need a printed (hard copy) version of pages Ia-4-2 through Ia-4-25 to complete this lab. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.

Step Two:

Bring the printed copy of the lab with you on Monday, April 14 (section 01) *or* **Wednesday, April 16 (section H1.)** You will need to create and submit four computer generated graphs with this report, plus you need to submit additional page(s) showing detailed calculations of your work for this lab. Include your name on page I-4-25!

Step Three:

Complete the lab work and calculations on your own, then **turn it in your lab** (page Ia-4-25 <u>*plus*</u> the graphs *and* work page(s) *only* to avoid a point penalty) **at the beginning of recitation to the instructor on Monday, April 21 (section 01)** *or* **Wednesday, April 23 (section H1.)** The graded lab will be returned to you the following week during recitation.

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

Acid and Base Titrations - Equation Guide

Strong Acid + Strong Base: *(SA + SB)*

Initial Region: $\mathbf{pH = -\log(n_{sa} / V_{sa})}$ *or* $\mathbf{pH = -\log(C_{sa})}$

Pre-Equivalence Region: $\mathbf{pH} = \mathbf{-log}\left(\frac{n_{sa}-n_{sb}}{V_{sa}+V_{sb}}\right)$ *or* $\mathbf{pH} = \mathbf{-log}\left(\frac{n_{sa}-n_{sb}}{V_{total}}\right)$

Equivalence: $\mathbf{pH = 7}$

Post-Equivalence Region: $\mathbf{pH} = \mathbf{14 + log}\left(\frac{n_{sb}-n_{sa}}{V_{sa}+V_{sb}}\right)$ *or* $\mathbf{pH} = \mathbf{14 + log}\left(\frac{n_{sb}-n_{sa}}{V_{total}}\right)$

Strong Base + Strong Acid: *(SB + SA)*

Initial Region: $\mathbf{pH = 14 + \log(n_{sb} / V_{sb})}$ *or* $\mathbf{pH = 14 + \log(C_{sb})}$

Pre-Equivalence Region: $\mathbf{pH} = \mathbf{14 + log}\left(\frac{n_{sb}-n_{sa}}{V_{sa}+V_{sb}}\right)$ *or* $\mathbf{pH} = \mathbf{14 + log}\left(\frac{n_{sb}-n_{sa}}{V_{total}}\right)$

Equivalence: $\mathbf{pH = 7}$

Post-Equivalence Region: $\mathbf{pH} = \mathbf{-log}\left(\frac{n_{sa}-n_{sb}}{V_{sa}+V_{sb}}\right)$ *or* $\mathbf{pH} = \mathbf{-log}\left(\frac{n_{sa}-n_{sb}}{V_{total}}\right)$

Weak Acid + Strong Base: *(WA + SB)*

Initial Region: $\mathbf{pH} = \mathbf{-log}\sqrt{K_a \cdot \frac{n_{wa}}{V_{wa}}}$ *or* $\mathbf{pH} = \mathbf{-log}\sqrt{K_a \cdot C_{wa}}$

Pre-Equivalence Region: $\mathbf{pH} = \mathbf{p}K_a\mathbf{ + log}\left(\frac{n_{sb}}{n_{wa}-n_{sb}}\right)$

Half-Equivalence Region: $\mathbf{pH = pK_a}$

Equivalence: $\mathbf{pH} = \mathbf{14 + log}\sqrt{\frac{K_w}{K_a} \cdot \frac{n_{wa}}{\left(V_{wa}+V_{sb}\right)}}$ *or* $\mathbf{pH} = \mathbf{14 + log}\sqrt{K_b \cdot C_{wb}}$

Post-Equivalence Region: $\mathbf{pH} = \mathbf{14 + log}\left(\frac{n_{sb}-n_{wa}}{V_{sb}+V_{wa}}\right)$ *or* $\mathbf{pH} = \mathbf{14 + log}\left(\frac{n_{sb}-n_{wa}}{V_{total}}\right)$

Continued on next page

Weak Base + Strong Acid: *(WB + SA)*

Initial Region: $\mathbf{pH = 14 + \log}\sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}}$ *or* $\mathbf{pH = 14 + \log}\sqrt{K_b \cdot C_{wb}}$

Pre-Equivalence Region: $\mathbf{pH = p}K_a \mathbf{+ \log}\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right)$

Half-Equivalence Region: $\mathbf{pH = pK_a}$

Equivalence: $\mathbf{pH = -\log}\sqrt{\frac{K_w}{K_b} \cdot \frac{n_{wb}}{\left(V_{wb} + V_{sa}\right)}}$ *or* $\mathbf{pH = -\log}\sqrt{K_a \cdot C_{wa}}$

Post-Equivalence Region: $\mathbf{pH = -\log}\left(\frac{n_{sa} - n_{wb}}{V_{sa} + V_{wb}}\right)$ *or* $\mathbf{pH = -\log}\left(\frac{n_{sa} - n_{wb}}{V_{total}}\right)$

Guide to Symbols

n = moles
V = volume (L)
C = concentration (M or mol/L)
sa = strong acid
sb = strong base
wa = weak acid
wb = weak base

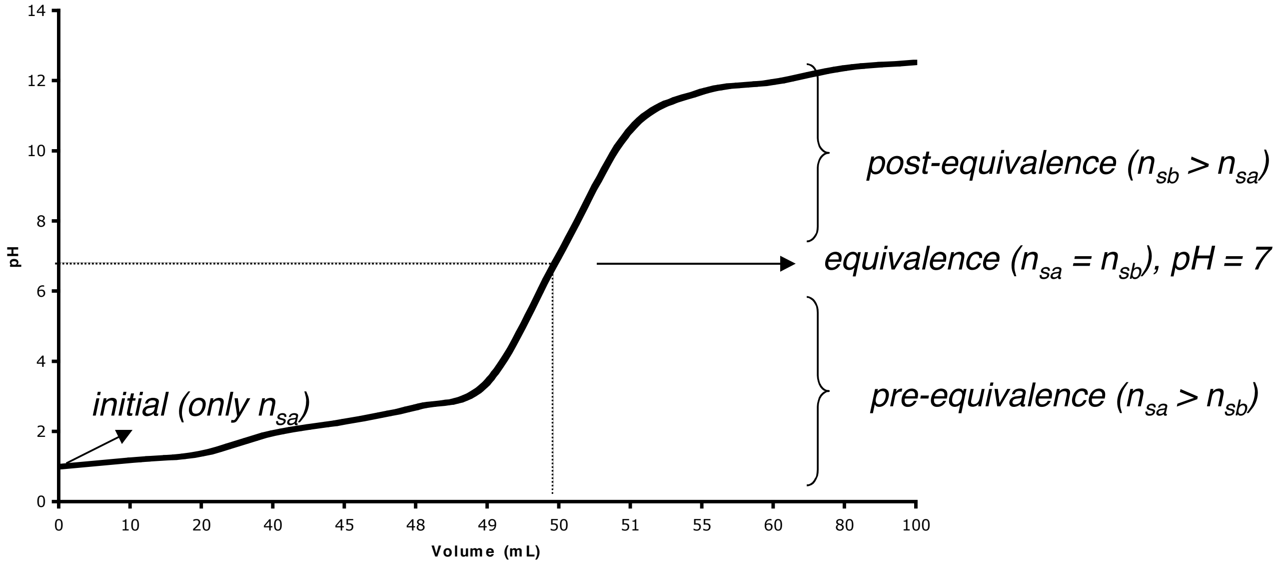
K_a = acid dissociation constant for a weak acid
$\mathbf{pK_a = -\log K_a}$
$\mathbf{K_a = 10^{-pKa}}$

K_b = base dissociation constant for a weak base
$\mathbf{pK_b = -\log K_b}$
$\mathbf{K_b = 10^{-pKb}}$

$\mathbf{K_w = 10^{-14}}$ = autoionization constant for water at 25 ˚C
Also, $\mathbf{K_w = [H_3O^+]*[OH^-] = K_a*K_b = 10^{-14}}$

$\mathbf{pH = -\log [H_3O^+]}$
$\mathbf{pOH = -\log [OH^-]}$
$\mathbf{14 = pH + pOH = pK_a + pK_b}$

Strong Acid + Strong Base Titration - *Overview*



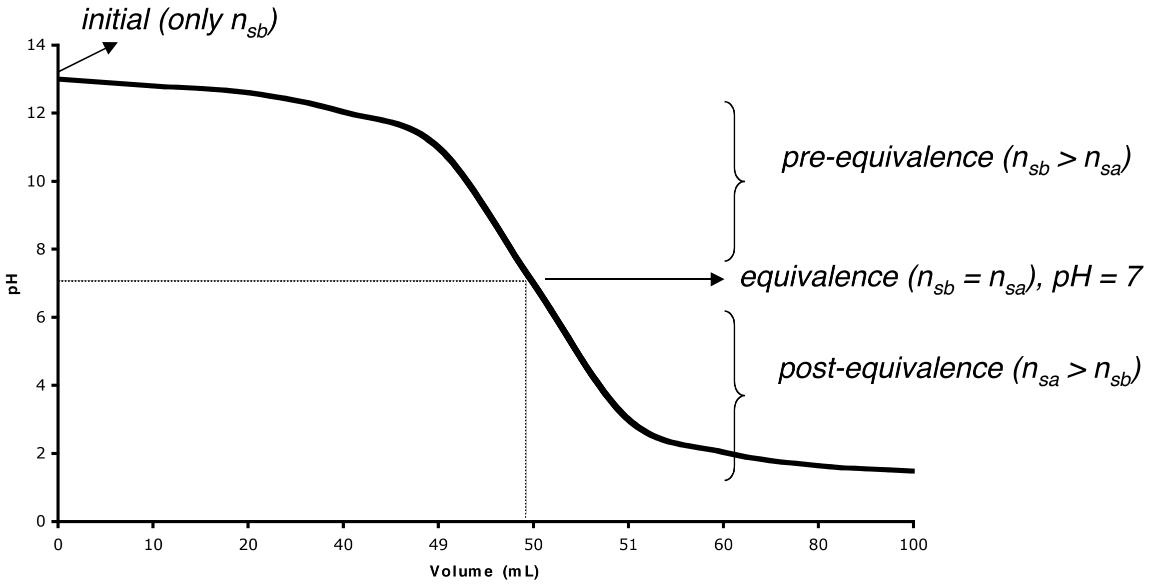
Initial: $\mathrm{pH} = -\log [n_{sa} / V_{sa}]$

Pre-equivalence: $\mathrm{pH} = -\log\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

Equivalence: pH = 7 (neutral salt + water)

Post-equivalence: $\mathrm{pH} = 14 + \log\left(\dfrac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$

Strong Base + Strong Acid Titration - *Overview*



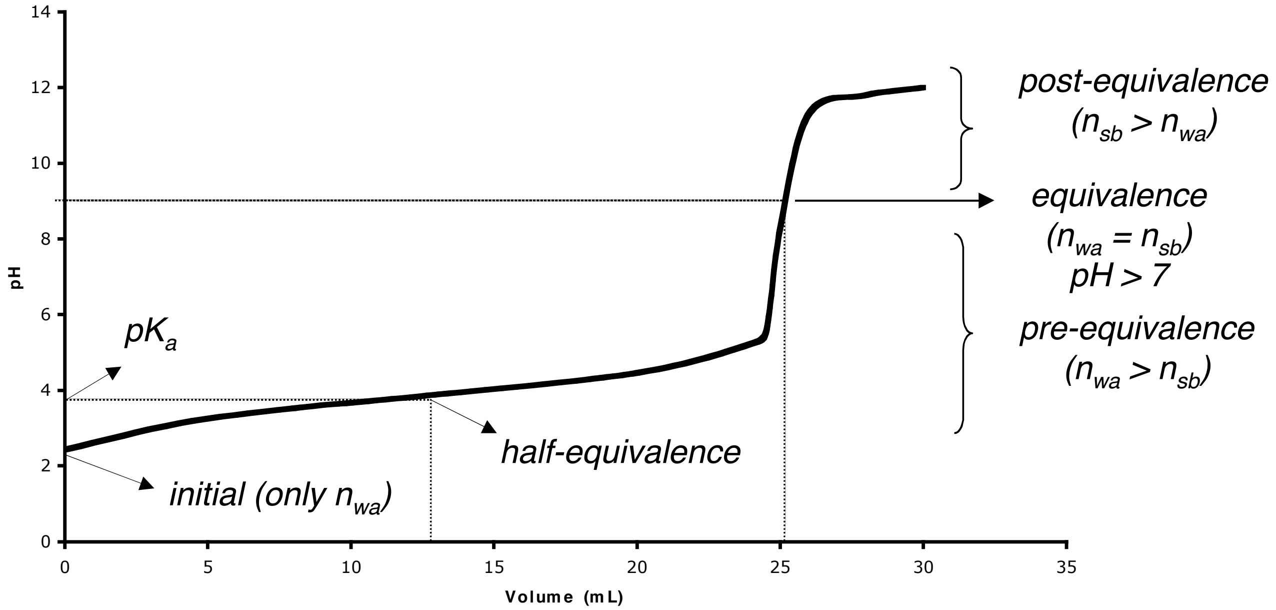
Initial: $\text{pH} = 14 + \log\,[n_{sb} / V_{sb}]$

Pre-equivalence: $$\text{pH} = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$$

Equivalence: pH = 7 (neutral salt + water)

Post-equivalence: $$\text{pH} = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$$

Weak Acid + Strong Base Titration - *Overview*



s

Initial:

$$pH = -\log\sqrt{K_a C_{wa}}$$

Pre-equivalence:

$$pH = pK_a + \log\left(\frac{n_{sb}}{n_{wa} - n_{sb}}\right)$$

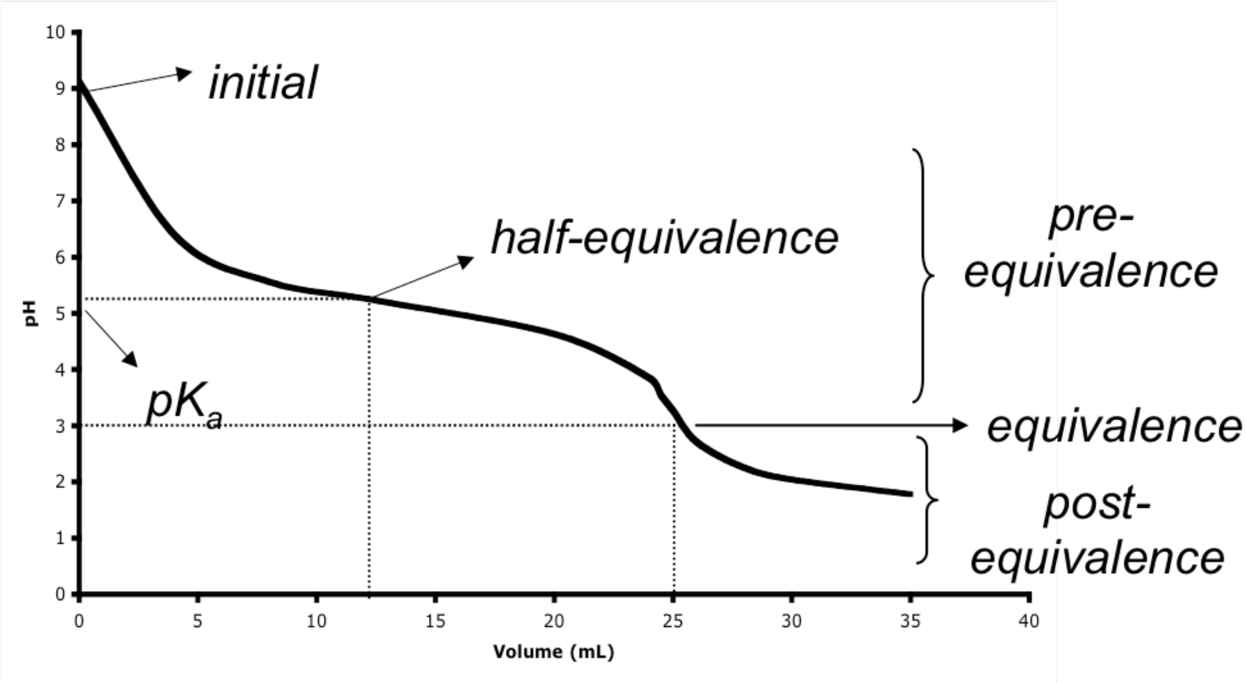
Equivalence:

$$pH = 14 + \log\sqrt{\left(\frac{K_w}{K_a}\right)\left(\frac{n_{wa}}{V_{wa} + V_{sb}}\right)}$$

Post-equivalence:

$$pH = 14 + \log\left(\frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right)$$

Weak Base + Strong Acid Titration - *Overview*



Initial:

$$pH = 14 + \log\sqrt{K_b C_{wb}}$$

Pre-equivalence:

$$pH = pK_a + \log\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right)$$

Equivalence:

$$pH = -\log\sqrt{\left(\frac{K_w}{K_b}\right)\left(\frac{n_{wb}}{V_{wb} + V_{sa}}\right)}$$

Post-equivalence:

$$pH = -\log\left(\frac{n_{sa} - n_{wb}}{V_{sa} + V_{wb}}\right)$$

CH 223 Guide to Acid and Base Titration Calculations

Acid and base titrations can be a challenging concept for students to conquer in CH 223. This handout will help prepare you for the types of problems associated with titrations.

A **titration** is an experimental procedure whereby a solution (usually either acidic or basic) is added dropwise to a second solution (usually either acidic or basic.) One solution will be acidic while the other will be basic. The solution that is added dropwise is called the **titrant**. Titrations are often graphed using **pH** as the y-axis and **Volume of Titrant (mL)** as the x-axis. Sometimes a second y-axis is used to plot the first derivative; we shall explore this concept in the labs during CH 223.

pH is defined as the negative log of the hydronium concentration, i.e. **pH = - log [H_3O^+]**. All of the calculations given below reflect this basic idea. Values of pH less than seven indicate acidic conditions, while pH values greater than seven indicate basic conditions; a pH reading of 7 is neutral (neither acidic nor basic). Weak acids, weak bases, strong acids and strong bases require different formulas to find the concentration of [H_3O^+]; hence, there are different mathematical approaches to titrations depending on the substituents being titrated. We shall concern ourselves only with **monoprotic** acids and bases - those that have only one equivalent of H_3O^+ or OH^- to offer.

We will study four monoprotic titration combinations:

- **Strong acid titrated with strong base:** the pH is initially acidic but becomes more basic as the strong base titrant is added
- **Strong base titrated with strong acid:** the pH is initially basic but becomes more acidic as the strong acid titrant is added
- **Weak acid titrated with strong base:** the pH is initially somewhat acidic but becomes more basic as the strong base titrant is added
- **Weak base titrated with strong acid:** the pH is initially somewhat basic but becomes more acidic as the strong acid titrant is added

Weak acid + weak base titration combinations require an intensive analysis of K_a and K_b constants and are of limited versatility; hence, we will cover only the first four types of titrations.

Before you begin calculations for *any* titration in CH 223, do the following:

1) Determine if solution to be titrated contains an acid or a base, and determine if it is strong or weak.
2) Determine if the titrant is an acid or base and if it is weak or strong
3) If the solution contains a weak acid, find the K_a; if a weak base, find K_b .
4) Refer to the appropriate section:

- **Strong Acid** (solution) titrated with a **Strong Base**: **Section One**
- **Strong Base** (solution) titrated with a **Strong Acid**: **Section Two**
- **Weak Acid** (solution) titrated with a **Strong Base**: **Section Three**
- **Weak Base** (solution) titrated with a **Strong Acid**: **Section Four**

Notes: **Weak acids with weak bases** and **weak bases with weak acids** will not be covered in CH 223. **Polyprotic acid and base titrations** will not be mathematically covered in CH 223 **Redox titrations** will be covered in the subsequent electrochemistry chapter. Additional information on pH calculations can be found in the Web-only handout "**A Closer Look at Titrations**" available on the CH 223 website

Section One: Strong Acid + Strong Base (SA + SB) Titration

Equivalence Point pH = 7 *neutral*

Before you begin:

Strong acids titrated with strong bases will neutralize each other at the equivalence point. Therefore, you should expect to see a neutral pH when the quantity of acid equals the quantity of base added.

Determine the following quantities:

$\mathbf{V_{sa}}$ = volume of strong acid initially present
$\mathbf{n_{sa}}$ = moles of strong acid (= $C_{sa} * V_{sa}$)
$\mathbf{C_{sb}}$ = concentration of strong base
$\mathbf{V_{sb}}$ = volume of strong base to reach equivalence point (= n_{sa} / C_{sb})

Analysis Section:

There are **four regions** in SA + SB titrations that require specific approaches to calculate the pH:

- *Initial Region:* **pH = - log (n_{sa} / V_{sa})**
  The pH will reflect the strong acid only - no strong base has been added.
- *Pre-Equivalence Region:* **pH = -log** $\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$
  The pH will reflect the remaining acid in solution after some neutralization with strong base.
  $n_{sa} > n_{sb}$ in this region.
- *Equivalence:* **pH = 7**
  $n_{sa} = n_{sb}$, so water and a neutral salt will be produced at this point.
- *Post-Equivalence Region:* **pH = 14 + log** $\left(\dfrac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right)$
  The pH will reflect the excess base remaining after neutralizing the strong acid.
  $n_{sb} > n_{sa}$ in this region.

Example: Titrate 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH. Determine the pH after 0.00, 10.0, 100. and 150. mL of NaOH has been added.

HNO_3 is a *strong acid*, NaOH is a *strong base*; the equivalence point pH = 7
$\mathbf{V_{sa}}$ = 50.0 mL = **0.0500 L**
$\mathbf{n_{sa}}$ = 0.200 M * 0.0500 L = **0.0100 mol**
$\mathbf{C_{sb}}$ = **0.100 M**
$\mathbf{V_{sb}}$ = 0.0100 mol / 0.100 M = 0.100 L = **100. mL NaOH to the equivalence point**

At 0.00 mL: Initial point: pH = - log (n_{sa} / V_{sa}) = - log (0.0100 mol / 0.0500 L) = **0.70**

The pH reflects only the strong acid; no strong base has been added at this point.

At 10.0 mL: Pre-equivalence point: $\text{pH} = -\log\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

At 10.0 mL, V_{sb} = **0.0100 L**, and n_{sb} = 0.0100 L * 0.100 M = **0.00100 mol**

$$\mathbf{pH = -log}\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right) \mathbf{= -log}\left(\frac{0.0100 - 0.00100}{0.0500 + 0.0100}\right) \mathbf{= 0.82}$$

Note: 10.0 mL < 100. mL (equivalence point), so this point is in the pre-equivalence region

At 100. mL: **Equivalence point, pH = 7**

At 100.0 mL, n_{sb} = 0.100 L * 0.100 M = 0.0100 mol = n_{sa}

Equal molar quantities of acid and base have been added; therefore,

$$HNO_3 + NaOH \rightarrow H_2O + NaNO_3$$

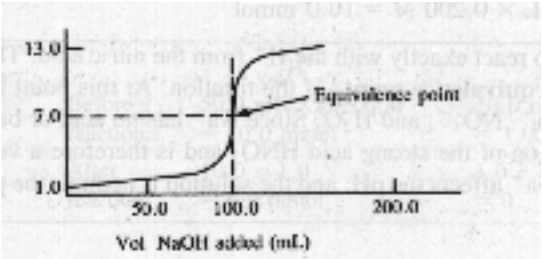
$NaNO_3$ is a neutral salt, and the pH of water is 7; therefore, the equivalence pH is **7**.

At 150. mL: Post-equivalence point: $\text{pH} = 14 + \log\left(\dfrac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right)$

At 150.0 mL, n_{sb} = 0.150 L * 0.100 M = **0.0150 mol**, which is larger than n_{sa}. This point lies in the post-equivalence region, so:

$$\text{pH} = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right) \mathbf{= 14 + log}\left(\frac{0.0150 - 0.0100}{0.150 + 0.0500}\right) \mathbf{= 12.40}$$

The **titration graph** for a strong acid + strong base would look like this:



Notice the sharp slope around the equivalence point region - this is indicative of strong acid + strong base titrations. Note that the equivalence point pH is 7.0 - this is also what we would expect for this type of titration. Knowing how to predict the type of titration from a graph can be of considerable assistance to you in CH 223.

<u>Section Two</u>: Strong Base + Strong Acid (SB + SA) Titration

Equivalence Point pH = 7 *neutral*

Analysis of this type of titration is very similar to the analysis for a Strong Acid + Strong Base (Section 1, above) *except* that the strong base will be dominant initially, followed by a slow erosion with a strong acid. Notice the subtle changes to the equations in this section when compared to section 1; you should see a pattern developing which can help you in your calculations.

Before you begin:

As in section 1, strong bases titrated with strong acids will neutralize each other at the equivalence point. Therefore, you should expect to see a neutral pH when the quantity of base equals the quantity of acid added.

<u>Determine the following quantities</u>:

$\mathbf{V_{sb}}$ = volume of strong base initially present
$\mathbf{n_{sb}}$ = moles of strong base (= C_{sb} * V_{sb})
$\mathbf{C_{sa}}$ = concentration of strong acid
$\mathbf{V_{sa}}$ = volume of strong acid to reach equivalence point (= n_{sb} / C_{sa})

<u>Analysis Section</u>:

There are **four regions** in SB + SA titrations that require specific approaches to calculate the pH:

- *Initial Region:* **pH = 14 + log ($\mathbf{n_{sb}}$ / $\mathbf{V_{sb}}$)**

  The pH will reflect the strong base only - no strong acid has been added.
  Note the presence of "14" in the equation; this is due to the fact that:

  $$pOH = -\log(n_{sb} / V_{sb})$$

  and

  $$14 = pH + pOH$$

  Combining these equations and solving for pH gives pH = 14 + log (n_{sb} / V_{sb}).

- *Pre-Equivalence Region:* **pH = 14 + log** $\left(\dfrac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right)$

  The pH will reflect the remaining base in solution after some neutralization with strong acid.
  $n_{sb} > n_{sa}$ in this region.

- *Equivalence:* **pH = 7**

  $n_{sb} = n_{sa}$, so water and a neutral salt will be produced at this point.

- *Post-Equivalence Region:* **pH = -log** $\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

  The pH will reflect the excess acid remaining after neutralizing the strong base.
  $n_{sa} > n_{sb}$ in this region.

Example: Titrate 100. mL of 0.500 M NaOH with 1.00 M HCl. Determine the pH after 0.00, 25.0, 50.0 and 80.0 mL of NaOH has been added.

NaOH is a *strong base*, HCl is a *strong acid*; the equivalence point pH = 7
$\mathbf{V_{sb}}$ = 100. mL = **0.100 L**
$\mathbf{n_{sb}}$ = 0.500 M * 0.100 L = **0.0500 mol**
$\mathbf{C_{sa}}$ = **1.00 M**
$\mathbf{V_{sa}}$ = 0.0500 mol / 1.00 M = 0.0500 L = **50.0 mL HCl to the equivalence point**

At 0.00 mL: Initial point: pH = 14 + log (n_{sb} / V_{sb}) = 14 + log (0.0500 mol / 0.100 L) = **13.70**

The pH reflects only the strong base; no strong acid has been added at this point.

At 25.0 mL: Pre-equivalence point: $\text{pH} = 14 + \log\left(\dfrac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right)$

At 25.0 mL, V_{sa} = **0.0250 L**, and n_{sa} = 0.0250 L * 1.00 M = **0.0250 mol**

$$\text{pH} = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right) = \mathbf{14 + log}\left(\frac{0.0500 - 0.0250}{0.100 + 0.0250}\right) = \mathbf{13.30}$$

Note: 25.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

Notice how there is little pH change upon adding this much acid. Strong base + strong acid pH curves change slowly until the equivalence point is reached, then the change becomes quite noticeable.

At 50.0 mL: **Equivalence point, pH = 7**
At 50.0 mL, n_{sa} = 0.0500 L * 1.00 M = 0.0500 mol = n_{sb}
Equal molar quantities of base and acid have been added; therefore,

$$\text{NaOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{NaCl}$$

NaCl is a neutral salt, and the pH of water is 7; therefore, the equivalence pH is **7**.

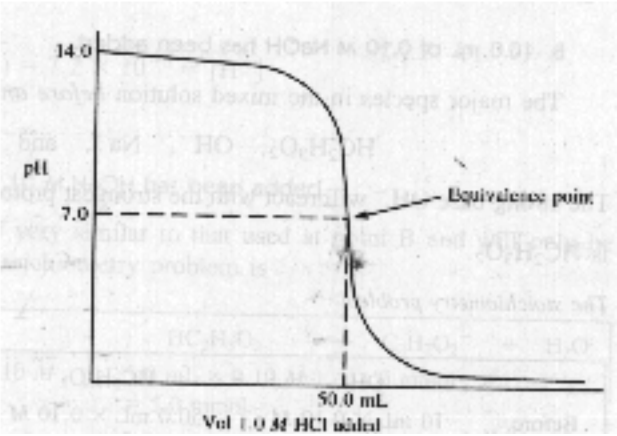
At 80.0 mL: Post-equivalence point: $\text{pH} = -\log\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

At 80.0 mL, n_{sa} = 0.0800 L * 1.00 M = **0.0800 mol**, which is larger than n_{sb}. This point lies in the post-equivalence region, so:

$$\text{pH} = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right) = \mathbf{-log}\left(\frac{0.0800 - 0.0500}{0.0800 + 0.100}\right) = \mathbf{0.78}$$

Notice how the pH changed rapidly between 25.0 mL of acid added (still quite basic) and 80.0 mL of acid added (where the pH is quite acidic). As the concentration of strong acids and bases increases, the titration curves will show a steeper equivalence point.

The **titration graph** for a strong base + strong acid would look like this:



As in section 1, notice the sharp slope around the equivalence point region - this is indicative of strong base + strong acid titrations. Note that the equivalence point pH is 7.0 - this is also what we would expect for this type of titration. At first, the NaOH dominated the titration, and the graph pH was quite basic. At the conclusion of the titration, HCl dominated and overcame the NaOH present in solution, and the pH became quite acidic. Remembering simple facts can aid your analysis of titrations in CH 223.

Section Three: Weak Acid + Strong Base (WA + SB) Titration

Equivalence Point pH > 7 *basic*

Weak acids and weak bases have incomplete ionization in solution, which is in marked contrast to their strong acid and strong base counterparts. For example, if we have a solution of 1.00 M HCl in water,

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

we would have 100% of the $HCl_{(aq)}$ converted to $H^+_{(aq)}$ and $Cl^-_{(aq)}$; no HCl would remain in solution.

If we had a solution of 1.00 M $HC_2H_3O_2$ in water,

$$HC_2H_3O_{2(aq)} \rightleftharpoons H^+_{(aq)} + C_2H_3O_2^{-1}{}_{(aq)}$$

we would have roughly 99% of the $HC_2H_3O_2$ still present in solution; less than 1% of the $HC_2H_3O_{2(aq)}$ would ionize into $H^+_{(aq)}$ and $C_2H_3O_2^-{}_{(aq)}$. Weak acids and weak bases do not ionize completely in solution. Recall that if $HC_2H_3O_2$ is our weak acid, $C_2H_3O_2^-{}_{(aq)}$ will be the **conjugate base** in this system. Strong acids and bases do not have effective conjugate acids or bases.

To account for the discrepancy in ionization behavior, we will use the **acid equilibrium constant, K_a**, and the **base equilibrium constant, K_b**, in our calculations. Recall that K_a and K_b are related to K_w, the autoionization of water constant, by the following expression:

$$K_w = K_a * K_b$$

To speed our calculations when the weak acid or weak base is present in excess, we can use the **Henderson-Hasselbalch equation**. We will use a slightly modified form in this section, but the generic equation is:

$$pH = pK_a + \log\frac{[\text{Conj. base}]}{[\text{acid}]}$$

where pH = pH of system

$pK_a = -\log K_a$ = - log (acid dissociation constant for weak acid in buffer)

[Conj. base] = concentration *or* moles of base in solution

[acid] = concentration *or* moles of weak acid in solution

The Henderson-Hasselbalch equation tells us that when the moles of the strong base added equal one-half the moles of weak acid initially present (i.e. $\frac{1}{2}\, n_{wa} = n_{sb}$), a special condition occurs; this point is called the **half-equivalence point**, and pH = pK_a here. Therefore, we need to add an additional region to our calculations, the **half-equivalence region**.

Before you begin: Determine the following quantities:

$\mathbf{V_{wa}}$ = volume of weak acid initially present

$\mathbf{n_{wa}}$ = moles of weak acid (= $C_{wa} * V_{wa}$)

$\mathbf{K_a}$ = acid dissociation constant for the weak acid

$\mathbf{pK_a}$ = - log K_a (this is a just a unitless number)

$\mathbf{C_{sb}}$ = concentration of strong base

$\mathbf{V_{sb}}$ = volume of strong base to reach equivalence point (= n_{wa} / C_{sb})

Also remember that at room temperature, $\mathbf{K_w = 10^{-14}}$

Analysis Section: There are **five regions** in WA + SB titrations in which to calculate the pH:

- *Initial Region:* **pH = -log**$\sqrt{K_a \cdot \frac{n_{wa}}{V_{wa}}}$

The pH will reflect the weak acid only - no strong base has been added. Recall that for weak acids,

$$[H_3O^+] = \sqrt{K_a \cdot C_{wa}}$$

and $C_{wa} = n_{wa} / V_{wa}$, just as pH = - log $[H_3O^+]$.

- *Pre-Equivalence Region:* $\mathbf{pH = p}K_a \mathbf{+ log} \left(\frac{n_{sb}}{n_{wa} - n_{sb}} \right)$

Because $n_{wa} > n_{sb}$ in this region, the pH will be affected by two factors: 1) the remaining weak acid in the solution, and 2) the *conjugate base* present upon addition of strong base. For weak acids HA reacting with strong base NaOH,

$$HA + NaOH \rightarrow HOH + Na^+ + A^-$$

The species A^- is the *conjugate base* of the weak acid HA, and it will react with water to re-form the weak acid:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

The generation of OH^- from the conjugate base will affect pH.

Fortunately, the weak acid / conjugate base system can be treated like a ***buffer***; hence, the usefulness of the Henderson-Hasselbalch equation. Recall that the Henderson-Hasselbalch equation is

$$\mathrm{pH = pK_a + log \frac{[Conj.\ base]}{[acid]}}$$

[Conj. base] and [acid] can be re-written as n_{sb} and $(n_{wa} - n_{sb})$, respectively*, or

$$\mathrm{pH = pK_a + log \frac{n_{sb}}{n_{wa} - n_{sb}}}$$

* *Why?* OK, here goes: for every mole of conjugate base created, an equal number of moles of strong base must be added, so [Conj. base] = n_{sb}. Also, the moles of weak acid present in solution will depend on how many moles of strong base have been added, so [acid] = $(n_{wa} - n_{sb})$.

Note that there is **no volume dependence in the pre-equivalence region**; you need not calculate total volume, etc. in this region *if* using the Henderson-Hasselbalch equation.

- *Half-Equivalence Region:* **pH = pK_a**

At half-equivalence, $\frac{1}{2} n_{wa} = n_{sb}$, and the log term in the pre-equivalence equation goes to zero (log 1 = 0). Note that *you can predict the pH of any weak acid system at half-equivalence by calculating the pK_a!*

- *Equivalence:* $\mathbf{pH = 14 + log}\sqrt{\frac{K_w}{K_a} \cdot \frac{n_{wa}}{(V_{wa} + V_{sb})}}$

At the equivalence point, $n_{wa} = n_{sb}$, and the only factor affecting pH is the conjugate base (see discussion on pre-equivalence, above.) To find $[OH^-]$ for a weak base, use:

$$[OH^-] = \sqrt{K_b \cdot C_{wb}} = \sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}}$$

For every mole of weak acid, an equal number of moles of conjugate base are created; hence, $n_{cb} = n_{wa}$.
The term V_{cb} must take into account the total volume present in solution, hence, $V_{cb} = V_{wa} + V_{sb}$.
K_b can be rewritten as K_w / K_a.
Converting $[OH^-]$ to pH provides the necessary equation

$$pH = 14 + \log\sqrt{\frac{K_w}{K_a} \cdot \frac{n_{wa}}{(V_{wa} + V_{sb})}}$$

Note that in titrations of weak acids with strong bases, the equivalence point pH will be affected by the pH of the conjugate base only; no weak acid remains in solution. Therefore, expect basic pH values at the equivalence point in weak acid + strong base titrations.

- *Post-Equivalence Region:* $\mathbf{pH = 14 + log}\left(\frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right)$

The pH will reflect the excess strong base remaining after neutralizing the weak acid. ($n_{sb} > n_{wa}$)
Note that the contribution of the *conjugate base* will have no appreciable effect on the pH assuming even a small portion of strong base is present in solution; therefore, it is omitted from the calculation.

Example: Titrate 50.0 mL of 0.100 M $HC_2H_3O_2$ ($K_a = 1.80 \times 10^{-5}$) with 0.100 M NaOH. Determine the pH after 0.00, 10.0, 25.0, 40.0, 50.0 and 60.0 mL of NaOH has been added.

$HC_2H_3O_2$ is a *weak acid*, NaOH is a *strong base*; the equivalence point should be *basic*
$\mathbf{V_{wa}}$ = 50.0 mL = **0.0500 L**
$\mathbf{n_{wa}}$ = 0.100 M * 0.0500 L = **0.00500 mol**
$\mathbf{C_{sb}}$ = **0.100 M**
$\mathbf{V_{sb}}$ = 0.00500 mol / 0.100 M = 0.0500 L = **50.0 mL NaOH to the equivalence point**
The **half-equivalence point** will be reached at (50.0 mL / 2) or **25.0 mL NaOH**
$\mathbf{pK_a}$ = - log K_a = - log (1.80×10^{-5}) = **4.74**

At 0.00 mL: Initial point:

$$pH = -\log\sqrt{K_a \cdot \frac{n_{wa}}{V_{wa}}} = \mathbf{-log}\sqrt{1.80\ \mathbf{x}\ \mathbf{10}^{-5} \cdot \frac{0.00500}{0.0500}} = \mathbf{2.87}$$

The pH reflects only the weak acid; no strong base has been added at this point.

Note how the initial pH of a weak acid is considerably more basic than the initial pH of a strong acid; this is due to the incomplete ionization of the weak acid (and the resulting dependency on K_a.)

At 10.0 mL: Pre-equivalence point:

$$\text{pH} = \text{p}K_a + \log\left(\frac{n_{sb}}{n_{wa} - n_{sb}}\right) = \mathbf{4.74 + log}\left(\frac{0.00100}{0.00500 - 0.00100}\right) = \mathbf{4.14}$$

At 10.0 mL, V_{sb} = **0.0100 L**, and n_{sb} = 0.0100 L * 0.100 M = **0.00100 mol**
Note: 10.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

At 25.0 mL: Half-equivalence point: $\text{pH} = \text{p}K_a$ = **4.74**

This is a simple calculation but one which gives tremendous insight into the system being studied.

At 40.0 mL: Pre-equivalence point:

$$\text{pH} = \text{p}K_a + \log\left(\frac{n_{sb}}{n_{wa} - n_{sb}}\right) = \mathbf{4.74 + log}\left(\frac{0.00400}{0.00500 - 0.00400}\right) = \mathbf{5.34}$$

At 40.0 mL, V_{sb} = **0.0400 L**, and n_{sb} = 0.0400 L * 0.100 M = **0.00400 mol**
Note: 40.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

At 50.0 mL: Equivalence point:

$$\text{pH} = 14 + \log\sqrt{\frac{K_w}{K_a} \cdot \frac{n_{wa}}{(V_{wa} + V_{sb})}} = \mathbf{14 + log}\sqrt{\frac{\mathbf{10^{-14}}}{\mathbf{1.8 \times 10^{-5}}} \cdot \frac{0.00500}{(0.0500 + 0.0500)}} = \mathbf{8.72}$$

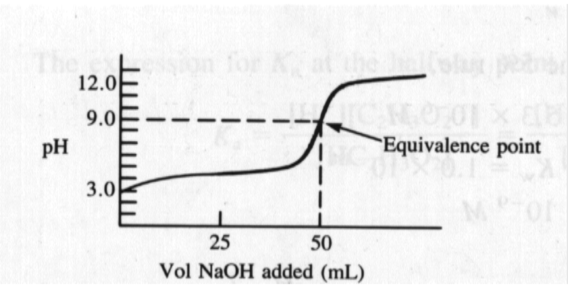
Note that this equation looks somewhat nasty, but really it's just a good old "plug and chug" equation. *Notice* how the equivalence pH is basic as predicted.

At 60.0 mL: Post-equivalence point:

$$\text{pH} = 14 + \log\left(\frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right) = \mathbf{14 + log}\left(\frac{0.00600 - 0.00500}{0.0600 + 0.0500}\right) = \mathbf{11.96}$$

At 60.0 mL, n_{sb} = 0.0600 L * 0.100 M = **0.00600 mol**, which is larger than n_{wa}. This point lies in the post-equivalence region.

The **titration graph** for a weak acid + strong base would look like the diagram below:



Note that the equivalence point is basic in a weak acid + strong base titration, a result of the conjugate base of the weak acid. Also note how the slope around the equivalence point is not as steep as it was when strong acids and bases were mixed together.

Section Four: Weak Base + Strong Acid (WB + SA) Titration

Equivalence Point pH < 7 *acidic*

As discussed in section three (WA + SB), weak acids and bases do not ionize completely in solution. For example, if we had a solution of 1.00 M NH_3 (ammonia, a weak base) in water,

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

we would have roughly 99% of the ammonia still present in solution; less than 1% of the $NH_{3(aq)}$ would ionize with water into $NH_4^+{}_{(aq)}$ and $OH^-{}_{(aq)}$. Recall that $NH_4^+{}_{(aq)}$ will be the **conjugate acid** in this system. This lack of complete ionization forces a dependency upon the **base equilibrium constant, K_b**, in our calculations.

As before, to speed our calculations when the weak base is present in excess, we can use the **Henderson-Hasselbalch equation**. We will use a slightly modified form for this section. The **half-equivalence point** will also be of use to use just as it was in the WA + SB titration.

Before you begin:

Determine the following quantities:

$\mathbf{V_{wb}}$ = volume of weak base initially present
$\mathbf{n_{wb}}$ = moles of weak base (= $C_{wb} * V_{wb}$)
$\mathbf{K_b}$ = base dissociation constant for the weak base
$\mathbf{pK_b}$ = - log K_b (this is a just a unitless number)
$\mathbf{C_{sa}}$ = concentration of strong acid
$\mathbf{V_{sa}}$ = volume of strong acid to reach equivalence point (= n_{wb} / C_{sa})
Also remember that at room temperature, $\mathbf{K_w = 10^{-14}}$

Analysis Section:

There are **five regions** in WB + SA titrations that require specific approaches to calculate the pH:

- *Initial Region:* $\mathbf{pH = 14 + \log\sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}}}$

The pH will reflect the weak base only - no strong acid has been added. Recall that for weak bases,

$$[OH^-] = \sqrt{K_b \cdot C_{wb}}$$

and $C_{wb} = n_{wb} / V_{wb}$. Recall that pOH = - log $[OH^-]$ and that pH + pOH = 14; therefore,

$$\mathbf{pH = 14 + \log\sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}}}$$

- *Pre-Equivalence Region:* This region uses a modified version of the Henderson-Hasselbalch equation to calculate pH:

$$\mathbf{pH = p}K_a \mathbf{+ log}\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right)$$

Because $n_{wb} > n_{sa}$ in this region, the pH will be affected by two factors: 1) the remaining weak base in the solution, and 2) the *conjugate acid* present upon addition of strong acid. For a weak base A^- reacting with strong acid HCl,

$$A^- + HCl \rightarrow HA + Cl^-$$

The species HA is the *conjugate acid* of the weak base A^-, and it will react with water to re-form the weak acid:

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

The generation of H_3O^+ from the conjugate acid will affect pH.

As in the weak acid / strong base scenario, the weak base / conjugate acid system can be treated like a ***buffer***; hence, the usefulness of the Henderson-Hasselbalch equation. Recall that the Henderson-Hasselbalch equation is

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\text{Conj. base}]}{[\text{acid}]}$$

We will modify the Henderson-Hasselbalch equation to our weakly basic system. [Conj. base] and [acid] can be re-written as $(n_{wb} - n_{sa})$ and n_{sa}, respectively*, and since $pK_a + pK_b = 14$, we can re-write our equation as

$$\mathbf{pH = p}K_a \mathbf{+ log}\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right)$$

* *Why?* OK, here goes: for every mole of conjugate acid created, an equal number of moles of strong acid must be added, so [acid] = n_{sa}. Also, the moles of weak base present in solution will depend on how many moles of strong acid have been added, therefore [Conj. base] is $(n_{wb} - n_{sa})$.

Note that there is **no volume dependence in the pre-equivalence region**; you need not calculate total volume, etc. in this region *if* using the Henderson-Hasselbalch equation.

- *Half-Equivalence Region:* **pH = pK$_a$**

At half-equivalence, $\frac{1}{2}\, n_{wb} = n_{sa}$, and the log term in the pre-equivalence equation goes to zero (log 1 = 0). Note that *you can predict the pOH of any weak base system at half-equivalence by calculating the pK_b or the pH via pK_a!* Converting to pH requires a simple but necessary calculation.

- *Equivalence:* **pH = -log**$\sqrt{\frac{K_w}{K_b}\cdot\frac{n_{wb}}{\left(V_{wb}+V_{sa}\right)}}$

At the equivalence point, $n_{wb} = n_{sa}$, and the only factor affecting pH is the conjugate acid (see discussion on pre-equivalence, above.) To find $[H_3O^+]$ for a weak acid:

$$[H_3O^+] = \sqrt{K_a \cdot C_{wa}} = \sqrt{K_a \cdot \frac{n_{wa}}{V_{wa}}}$$

For every mole of weak base, an equal number of moles of conjugate acid are created; hence, $n_{wa} = n_{wb}$.
The term V_{wa} must take into account the total volume present in solution, hence, $V_{wa} = V_{wb} + V_{sa}$.
K_a can be rewritten as K_w / K_b.
Converting $[H_3O^+]$ to pH provides the necessary equation

$$\text{pH} = -\log\sqrt{\frac{K_w}{K_b}\cdot\frac{n_{wb}}{\left(V_{wb}+V_{sa}\right)}}$$

Note that in titrations of weak bases with strong acids, the equivalence point pH will be affected by the pH of the conjugate acid only; no weak base or strong acid remains in solution. Therefore, expect acidic pH values at the equivalence point in weak base + strong acid titrations.

- *Post-Equivalence Region:* **pH = -log**$\left(\frac{n_{sa}-n_{wb}}{V_{sa}+V_{wb}}\right)$

The pH will reflect the excess strong acid remaining after neutralizing the weak base.
$n_{sa} > n_{wb}$ in this region.
Note that the contribution of the *conjugate acid* will have no appreciable effect on the pH assuming even a small portion of strong acid is present in solution; therefore, it is omitted from the calculation.

Example: Titrate 100. mL of 0.0500 M NH_3 ($K_b = 1.80*10^{-5}$) with 0.100 M HCl. Determine the pH after 0.00, 10.0, 25.0, 50.0 and 60.0 mL of HCl has been added.

NH_3 is a *weak base*, HCl is a *strong acid*; the equivalence point should be *acidic*
$\mathbf{V_{wb}}$ = 100. mL = **0.100 L**
$\mathbf{n_{wb}}$ = 0.0500 M * 0.100 L = **0.00500 mol**
$\mathbf{C_{sa}}$ = **0.100 M**
$\mathbf{V_{sa}}$ = 0.00500 mol / 0.100 M = 0.0500 L = **50.0 mL HCl to the equivalence point**
The **half-equivalence point** will be reached at (50.0 mL / 2) or **25.0 mL HCl**
$\mathbf{pK_a}$ = - log (K_w / K_b) = - log ($10^{-14} / 1.80*10^{-5}$) = **9.26**

At 0.00 mL: Initial point:

$$\text{pH} = 14 + \log\sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}} = \mathbf{14 + \log}\sqrt{1.8\ \mathbf{x}\ \mathbf{10}^{-5}\cdot\frac{0.00500}{0.100}} = \mathbf{10.98}$$

The pH reflects only the weak base; no strong acid has been added at this point.

Note how the initial pH of a weak base is considerably more acidic than the initial pH of a strong base; this is due to the incomplete ionization of the weak base (and the resulting dependency on K_b.)

At 10.0 mL: Pre-equivalence point:

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right) = \mathbf{9.26 + log}\left(\frac{0.00500 - 0.00100}{0.00100}\right) = \mathbf{9.86}$$

At 10.0 mL, V_{sa} = **0.0100 L**, and n_{sa} = 0.0100 L * 0.100 M = **0.00100 mol**

Note: 10.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

At 25.0 mL: Half-equivalence point: pH = $\mathrm{p}K_a$ = 14 - $\mathrm{p}K_b$ = 14 - 4.74 = **9.26**

Although simple, this calculation gives tremendous insight into the system being studied.

At 50.0 mL: Equivalence point:

$$\mathrm{pH} = -\log\sqrt{\frac{K_w}{K_b}\cdot\frac{n_{wb}}{\left(V_{wb}+V_{sa}\right)}} = \mathbf{-log}\sqrt{\frac{\mathbf{10^{-14}}}{\mathbf{1.80\ x\ 10^{-5}}}\cdot\frac{0.00500}{\left(0.0500+0.100\right)}} = \mathbf{5.37}$$

Note that this equation looks somewhat nasty, but really it's just a good old "plug and chug" equation. All of the values have been calculated, and the application will become easier with time.

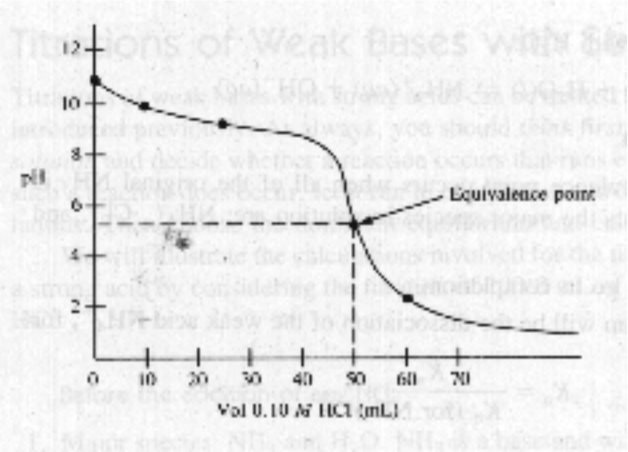
Notice how the equivalence point pH is acidic as predicted.

At 60.0 mL: Post-equivalence point:

$$\mathbf{pH = -log}\left(\frac{n_{sa} - n_{wb}}{V_{sa} + V_{wb}}\right) = \mathbf{-log}\left(\frac{0.00600 - 0.00500}{0.0600 + 0.100}\right) = \mathbf{2.20}$$

At 60.0 mL, n_{sa} = 0.0600 L * 0.100 M = **0.00600 mol**, which is larger than n_{wb}. This point lies in the post-equivalence region.

The **titration graph** for a weak base + strong acid would look like this:



Note that the equivalence point is acidic in a weak base + strong acid titration, a result of the conjugate acid of the weak base. Also note how the slope around the equivalence point is not as steep as it was when strong acids and bases were mixed together.

CH 223 Titration Calculations - *The Problems*

Exercises: *Complete these problems using the worksheet on the next page. Also, construct a graph of pH versus Volume of Titrant for each problem. Staple calculations to the back of the worksheet on separate paper. All pH calculations should be reported to the hundredths place.*

1. You wish to titrate 50.00 mL of a 0.100 M HCl solution with 0.100 M NaOH. Calculate the pH after the addition of 0.00 mL, 10.00 mL, 20.00 mL, 40.00 mL, 45.00 mL, 48.00 mL, 49.00 mL, 50.00 mL, 51.00 mL, 55.00 mL, 60.00 mL, 80.00 mL and 100.00 mL of NaOH. Plot the results of your calculations as pH versus mL of NaOH added.

2. You wish to titrate 38.00 mL of a 0.1680 M KOH solution with 0.1120 M HNO_3. Calculate the pH after the addition of 0.00 mL, 5.00 mL, 12.70 mL, 29.99 mL, 51.00 mL, 55.50 mL, 57.00 mL, 61.20 mL, 74.70 mL, 82.20 mL, 88.50 mL, 92.30 mL and 100.00 mL of HNO_3. Plot the results of your calculations as pH versus mL of HNO_3 added.

3. A 25.00 mL solution of 0.100 M lactic acid ($HC_3H_5O_3$, $pK_a = 3.85$) is titrated with 0.100 M LiOH. Calculate the pH after the addition of 0.00 mL, 4.00 mL, 8.00 mL, 12.50 mL, 20.00 mL, 24.00 mL, 24.50 mL, 25.00 mL, 26.00 mL, 28.00 mL, 30.00 mL, 35.00 mL and 40.00 mL of LiOH. Plot the results of your calculations as pH versus mL of LiOH added.

4. A student titrates 29.00 mL of 0.2250 M pyridine ($K_b = 1.7*10^{-9}$) with 0.3750 M HBr. Calculate the pH after the addition of 0.00 mL, 2.00 mL, 3.60 mL, 5.00 mL, 6.50 mL, 8.70 mL, 9.90 mL, 10.00 mL, 10.80 mL, 15.00 mL, 17.40 mL, 18.70 mL and 36.00 mL of HBr. Plot the results of your calculations as pH versus mL of HBr added.

CH 223 Titration Calculations *Answer Sheet*

Name: ______________________

Provide answers to the questions (found on the previous page) using the sheet below.

- **Report *all* pH values to the hundredths place**.
- ***Circle*** the **equivalence point** *and* the **half-equivalence point** (if appropriate) **volume** on the handout
- Include computer generated **graphs** (using Excel, etc.) of the titrations **and all necessary calculations** on separate paper **stapled** to the **back** of this handout (put this page on **top** for full credit!)

Question #1		***Question #2***		***Question #3***		***Question #4***	
Volume NaOH	**pH**	**Volume HNO_3**	**pH**	**Volume LiOH**	**pH**	**Volume HBr**	**pH**
0.00		0.00		0.00		0.00	
10.00		5.00		4.00		2.00	
20.00		12.70		8.00		3.60	
40.00		29.99		12.50		5.00	
45.00		51.00		20.00		6.50	
48.00		55.50		24.00		8.70	
49.00		57.00		24.50		9.90	
50.00		61.20		25.00		10.00	
51.00		74.70		26.00		10.80	
55.00		82.20		28.00		15.00	
60.00		88.50		30.00		17.40	
80.00		92.30		35.00		18.70	
100.00		100.00		40.00		36.00	

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CH 223 Spring 2025:

“Acid & Base Titrations *(in class)”* ***Lab*** *- Instructions*

Note: **This is the lab for section 01 and H1 of CH 223 only.**

- *If you are taking section W1 of CH 223*, please use this link: http://mhchem.org/q/5b.htm

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Step One:

Get a printed copy of this lab! You will need a printed (hard copy) version of pages Ia-5-2 through Ia-5-9 to complete this lab. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.

Step Two:

Bring the printed copy of the lab with you on Monday, April 21 (section 01) *or* **Wednesday, April 23 (section H1.)** During lab in room AC 2507, you will use these sheets (with the valuable instructions!) to gather data, all of which will be recorded in the printed pages below.

Step Three:

Complete the lab work and calculations on your own, then **turn it in** (pages Ia-5-5 through Ia-5-9 *only* to avoid a point penalty) **at the beginning of recitation to the instructor on Monday, April 28 (section 01)** *or* **Wednesday, April 30 (section H1.)** The graded lab will be returned to you the following week during recitation.

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

Acid & Base Titrations

During the next several labs you will perform titrations on acids and bases to determine various properties about these solutions. This first lab is designed as an introduction to titration with acids and bases. The focus of this lab will be to familiarize you with the Vernier computer system and to perform a titration using it. The program you use can be modified as needed in the following lab classes.

A **titration** is a process by which a solution of known concentration is quantitatively added to a solution of unknown concentration in order to determine its concentration. You will be using burets to perform the titrations. The titration **end point** or **equivalence point** is when stoichiometrically equivalent amounts of the two substances are present. Therefore, it is necessary to create a method for determining the endpoint of the titration. In an acid-base titration, the change in the acidity or pH of the solution is a convenient method to determine this equivalence point.

There are two methods to measure the pH of a solution. In the first method a chemical called an **indicator** is used that changes color upon a change in the acidity of the solution. Litmus and phenolphthalein are examples of common indicators. The second method is to use a **pH meter** to measure the pH of the solution as the titration proceeds.

In this lab you will use a Vernier interface with a pH probe to measure the $[H_3O^+]$ of the solution. The program will graph the progress of the titration as the titrant is added from the buret (measured with a drop counter.) A plot of the pH of a solution against the volume of titrant added is called a **titration curve**. From the titration curve, the equivalence point can be determined as the point of maximum slope. For an acid-base titration, the equivalence point occurs when moles of acid equal moles of base: $[H_3O^+] = [OH^-]$. Furthermore, the equivalence point will reveal whether the solution consists of a strong or weak acid.

For an acid, HA, in solution, the equilibrium constant K_a for the process can be determined:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \qquad K_a = \frac{[H_3O+][A^-]}{[HA]}$$

Recall that in solution, there is also a second equilibrium of concern:

$$\mathbf{2\,H_2O \rightleftharpoons H_3O^+ + OH^-, \qquad K_w = [H_3O^+][OH^-] = 1.00 * 10^{-14}}$$

For a **strong acid**, K_a is so large that the acid dissociates completely into H_3O^+ and A^- such that $[HA] = [H_3O^+]$ even in the untitrated state. At equivalence, the dissociation of water governs the pH, and the pH = 7.

For a **weak acid**, K_a is small and hence influences the pH. The initial pH of the solution will appear higher than that of a strong acid and the pH at the equivalence point is not 7. To calculate K_a, you will need to determine the pH halfway to the equivalence point. At the halfway point or **half equivalence point**, half of the acid has been titrated such that $[A^-] = [HA]$. This will reduce the equilibrium expression to $K_a = [H_3O^+]$ or **pH = pK_a**. Therefore, if the volume at the equivalence point is determined, the pH at half that volume will reveal pK_a.

PERFORMING THE EXPERIMENT - *Instructions*

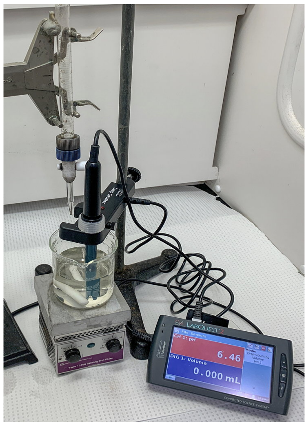
You will use a Vernier interface and equipment to titrate three acids using NaOH. Note the setup of the Vernier equipment carefully; you shall perform several similar titrations during this lab period and in the weeks to come. At the end, optionally upload your graphs (and maybe data files) to your email account and analyze them later at your convenience.

1. Obtain approximately 65 mL of NaOH solution in a 250 mL beaker.
2. Obtain a 25 or 50 mL buret and connect it to a ring stand using a buret clamp. Rinse the buret with a few mL of the NaOH and discard into a waste jar. Now fill the buret to the 0.00 mL line. Drain a small amount of NaOH solution into the 250 mL beaker so it fills the buret's tip. Use a disposable pipet to ensure the NaOH volume is still at 0.00 mL.
3. Connect the pH Sensor to CH 1 of the Vernier LabQuest 2 Interface. Lower the Drop Counter onto a ring stand and connect it to DIG 1. Choose **New** from the **File** menu.
4. ***Calibrate the Drop Counter*** so that a precise volume of titrant is recorded in units of milliliters.
    a. Choose **Sensors ► Calibrate ► Drop Counter** from the Sensors menu. *If you do not see the "Sensors" entry at the top, push the "Meter" icon in the upper left corner.*
        - *If you have previously calibrated the drop size* of your buret and want to continue with the same drop size, tap **Equation** after selecting the "Drop Counter" in the "Calibrate" menu. Enter the value for drops/mL. Select Done, then OK. Proceed directly to the next section.
        - If you want to perform a new calibration (i.e. if you change burets), continue with this step.

    b. Select **Calibrate Now**.
    c. Place a 10 mL graduated cylinder directly below the slot on the Drop Counter, lining it up with the tip of the buret.
    d. Open the valve on the buret. Slowly add NaOH from the buret at a slow rate (~1 drop every second). You should see the drops being counted on the screen.
    e. When the volume of NaOH solution added from the buret is between 3 and 9 mL, close the buret.
    f. Enter the precise Volume of NaOH to 0.01 mL. Select **Done**. **Record** the number of drops/mL displayed on the screen (**Sensors ► Calibrate ► Drop Counter** then **Equation**) for possible future use. Select OK.
    g. It's also recommended to **calibrate the pH meter (Sensors ► Calibrate ► pH Meter)**. Use a two point calibration (at pH of 4 and 10 using buffer solutions in small beakers.)
5. Discard the NaOH solution in the graduated cylinder and set it aside. Fill the NaOH in the buret to the 0.00 mL level.

6. Using a graduated cylinder, measure **5.00 mL HCl** (**record the concentration!**) into a 250 mL beaker. Add about 100 mL of water.

7. Assemble the apparatus.
    a. Place a magnetic stirrer under or near the ring stand with the buret. Place a stir bar in the 250 mL beaker with the HCl and place it on the magnetic stirrer.
    b. Rinse the pH sensor with water, then insert it through the large hole in the Drop Counter and attach it to the ring stand. Make sure the stir bar does not touch the bulb of the pH sensor.
    c. Adjust the positions of the Drop Counter and buret so they are both lined up. Test the positioning by releasing a few drops of NaOH; if the red light on the drop counter appears and disappears, all is well; if not, readjust the buret so the drops are counted. Also make sure the pH Sensor is just touching the bottom of the beaker.



8. Turn on the magnetic stirrer so that the stir bar is stirring at a fast rate, but not hitting the pH sensor bulb.

9. You are now ready to begin collecting data! Check to see that the pH value is **acidic** (you are starting with an acid.)

10. **Start data collection** by pressing the "start" button (the **green arrow** in the corner of the LabQuest.) No data will be collected until the first drop goes through the Drop Counter slot. Open the buret valve so that about 1 drop is released every 1 second or so. When the first drop passes through the Drop Counter slot, check the graph to see that the first data pair was recorded.

11. Continue watching your graph to see when a large increase in pH takes place—this will be the equivalence point of the reaction. When this jump in pH occurs, let the titration proceed for several more milliliters of titrant, then **stop data collection** (the **red square** in the corner) to view the graph of pH vs. volume. Make sure you see the "S" curve (or more if the acid is polyprotic.)

12. Dispose of the beaker contents in a waste jar, remembering not to put the stir bar in the waste jar.

13. **Examine the data** on the displayed graph of pH vs. volume (in mL) using your finger or the stylus to estimate the equivalence point volume and pH. **Record the pH value** in your notebook and **record the NaOH volume in mL** at the equivalence point. *Note:* if this is a weak acid graph, also record the half equivalence volume and the half equivalence pH value.

14. You are now done with Experiment #1 (HCl + NaOH). ☺

15. **Experiment #2** will be similar, but this time with **acetic acid**. Repeat the above procedure with HCl but substitute acetic acid for HCl (use the same volumes, etc.) Make sure to **rinse the pH meter with water before inserting it into a new solution.** Remember to record the acetic acid concentration!

16. **Experiment #3** will be similar, but this time with **phosphoric acid**. Repeat the above procedure with HCl but substitute phosphoric acid for HCl (use the same volumes, etc.) Remember to record the phosphoric acid concentration! Make sure your pH at the end of the titration if quite basic…. this is a polyprotic acid, and the graph should look quite different.

Use these instructions as you gather data and analyze three titrations.

Special note: we will be using these instructions during the next lab (Titration of Weak Acids), so bring these pages to that lab as well!

Acid & Base Titrations - *Worksheet*

YOUR NAME: ________________________ ***LAB PARTNER:*** __________________

Purpose: To explore acid-base pH titrations for three types of acid + strong base systems.

<u>Experiment #1</u>: HCl + NaOH

Determine the equivalence point volume and pH from the graph. Using the equivalence point volume and the exact concentration of the HCl, determine the **molarity of the pure** (initial) **NaOH solution** (i.e. before the NaOH reacted with the HCl.)

Equivalence point volume of NaOH (mL): ______________ Equivalence point pH: ______________

Concentration of HCl used in lab (M): ______________

Using the equivalence point volume and the exact concentration of the HCl, determine the **molarity of the pure** (initial) **NaOH solution** (i.e. before the NaOH reacted with the HCl.) *Show your work!*

HCl is a: strong acid strong base weak acid weak base *(Circle one)*

NaOH is a: strong acid strong base weak acid weak base *(Circle one)*

What *should* be the equivalence point pH be for this experiment?

less than 7 equal to 7 greater than 7 *(Circle one)*

Assume it takes 2.80 mL of 0.1100 M NaOH to titrate 5.00 mL of HCl. **Calculate the concentration of HCl using this data** (and show your work!)

Experiment #2: Acetic Acid - NaOH

Determine the equivalence point volume and pH from the graph. Based on the volume added at the equivalence point, **record the pH and volume at the half-equivalence point**. **Determine the K_a value based on the half equivalence point data**.

Equivalence point volume of NaOH (mL): ______________ Equivalence point pH: ______________

Half Equivalence point volume of NaOH (mL): __________ Half Equivalence point pH: __________

Experimental Ka of acetic acid: ______________________________ *Show work*

acetic acid is a: strong acid strong base weak acid weak base *(Circle one)*

What *should* be the equivalence point pH be for this experiment?

less than 7 equal to 7 greater than 7 *(Circle one)*

Why is the half-equivalence pH (and half-equivalence volume) important in this titration? Explain.

Acetic acid has a known K_a of 1.8×10^{-5} via the literature. Find the **percent error** for this experiment.
Recall: **Percent error = absolute value{(actual - experimental)/ actual}*100%**

Draw the Lewis structure of acetic acid showing all bonds and lone pair electrons:

Experiment #3: Phosphoric Acid - NaOH

Record the volume *and* pH values at the TWO equivalence points (first *and* second) for the phosphoric acid solution. (In most cases, you will not be able to observe the third equivalence point.) Use your data and/or graphs to determine the exact equivalence points.

Record the pH and volume at *each* half-equivalence point (first *and* second)**. Determine the value of K_{a1} and K_{a2} using the two half equivalence point values** on your graph. Note that to find K_{a2}, take the mid-point volume between the first equivalence point and the second equivalence point.

phosphoric acid is a: strong acid strong base weak acid weak base *(Circle one)*

From the graph, estimate the **first** equivalence volume: ________________ mL

From the graph, estimate the **first** equivalence pH: ________________

From the graph, estimate the **first** half-equivalence volume: ________________ mL

From the graph, estimate the **first** half-equivalence pH: ________________

Using this value, calculate the value of K_{a1} for phosphoric acid: ________________ *Show work*

Write the balanced equation used for K_{a1} of phosphoric acid

$H_3PO_4(aq)$ + $H_2O(l)$ $\rightleftharpoons$ ___________ + ____________________

Experiment #3: Phosphoric Acid - NaOH *Continued*

From the graph, estimate the **second** equivalence volume: ________________ mL

From the graph, estimate the **second** equivalence pH: ________________

From the graph, estimate the **second** half-equivalence volume: ________________ mL

From the graph, estimate the second half-equivalence pH: ________________

Using this value, calculate the value of K_{a2} for phosphoric acid: ________________ *Show work*

Write the balanced equation used for K_{a2} of phosphoric acid:

_____________ + $\mathbf{H_2O(l)}$ $\rightleftharpoons$ ______________ + ____________________

Postlab Questions:

1. If you titrate 100 mL of an unknown strong acid solution with 0.1 M NaOH, will the pH ever reach a value of 13? Explain.

2. What should the pH value be for the third half-equivalence point for phosphoric acid? Explain. Calculate what the exact value of pH should be by using the table of acid dissociation constants in problem set #2.

3. What is the molarity of an HCl solution if 25.00 mL of the acid solution required 42.68 mL of 0.2525 M NaOH solution to reach the equivalence point?

4. A student titrates 50.0 mL of a weak acid, HA, with 0.100 M NaOH. It requires 43.68 mL of 0.100 M NaOH to reach the equivalence point of the titration.
    a. Calculate the moles of HA present.
    b. Calculate the original (undiluted) concentration of the weak acid solution.
    c. It took 21.84 mL of 0.100 M NaOH to reach the half-equivalence point for this reaction, and the pH of the solution at this point was 6.00. Calculate the K_a for the weak acid.

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CH 223 Spring 2025:
"Titration of Weak Acids *(in class)"* ***Lab*** *- Instructions*

Note: **This is the lab for section 01 and H1 of CH 223 only.**

- *If you are taking section W1 of CH 223*, please use this link:
  http://mhchem.org/q/6b.htm

Step One:

Get a printed copy of this lab! You will need a printed (hard copy) version of pages Ia-6-3 through Ia-6-4 to complete this lab. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.
* ***Special Note:*** Also bring a printed copy of the "Acid and Base Titrations" instructions for the Vernier pH titration equipment (we will use these again this week.)

Step Two:

Bring the printed copy of the lab (and the Vernier instructions) with you on Monday, April 28 (section 01) *or* **Wednesday, April 30 (section H1.)** During lab in room AC 2507, you will use these sheets (with the valuable instructions!) to gather data, all of which will be recorded in the printed pages below.

Step Three:

Complete the lab work and calculations on your own, then **turn it in** (pages Ia-6-3 through Ia-6-4 *only* to avoid a point penalty) **at the beginning of recitation to the instructor on Monday, May 5 (section 01)** *or* **Wednesday, May 7 (section H1.)** The graded lab will be returned to you the following week during recitation.

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

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Titration of Weak Acids

Name:

Complete the following questions. All work must be shown to receive full credit.

Lab Partner(s):

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1. *Perform in the lab*

Select an unknown acid and titrate ***two samples*** of the acid per the guidelines in the "**Acid and Base Titration**" lab.

Measure approximately 0.5 g of the unknown acid sample using an analytical balance (record to 0.0001 g) and dissolve each sample in about 75 mL of water. Record the following information for each sample; show all work and include calculations.

[NaOH] (M): __________________	[NaOH] (M): __________________
<u>Sample #1</u> **Letter = _________**	**<u>Sample #2</u>** **Letter = _________**
Unknown sample (g): _________________	Unknown sample (g): _________________
Equivalence volume (mL): _________________	Equivalence volume (mL): _________________
Half-equivalence volume (mL): _________________	Half-equivalence volume (mL): _________________
Equivalence pH: _________________	Equivalence pH: _________________
Half-equivalence pH: _________________	Half-equivalence pH: _________________

---

2. *Lab Calculations: show all calculations on separate paper; include with your lab report*

mol unknown acid at equivalence: ______________	mol unknown acid at equivalence: ______________
molar mass unknown (g/mol): _________________	molar mass unknown (g/mol): _________________
K_a unknown acid: ________________________	K_a unknown acid: ________________________

Average K_a: _____________	Parts per thousand (K_a): __________
Average molar mass (g/mol): ______________	Parts per thousand (molar mass): _____________

3. Postlab question: *(Show all work after the problem.)*

   0.4998 g an unknown acid was placed in 75.00 mL of water.
   The unknown acid required 16.44 mL of 0.2001 M NaOH to reach equivalence.
   The pH at half equivalence was 3.86

K_a: _____________ **Molar mass of unknown (g/mol)**: __________

Volume NaOH to reach Half-equivalence (mL): _____________

Concentration of Unknown acid in original solution (M): ________________

CH 223 Spring 2025:

“Determination of K_{sp}, ΔG°, ΔH° and ΔS° for $Ca(OH)_2$”

(in class) ***Lab:*** *Instructions*

Note: **This is the lab for section 01 and H1 of CH 223 only.**

- *If you are taking section W1 of CH 223*, please use this link: http://mhchem.org/q/7b.htm

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Step One:

Get a printed copy of this lab! You will need a printed (hard copy) version of pages Ia-7-2 through Ia-7-12 to complete this lab. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.

Step Two:

Bring the printed copy of the lab with you on Monday, May 12 (section 01) *or* **Wednesday, May 14 (section H1.)** During lab in room AC 2507, you will use these sheets (with the valuable instructions!) to gather data, all of which will be recorded in the printed pages below.

Step Three:

Complete the lab work and calculations on your own, then **turn it in** (pages Ia-7-5 through Ia-7-12 *only* to avoid a point penalty) **at the beginning of recitation to the instructor on Monday, May 19 (section 01)** *or* **Wednesday, May 21 (section H1.)** The graded lab will be returned to you the following week during recitation.

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

Determination of K_{sp}, ΔG°, ΔH° and ΔS° for $Ca(OH)_2$

The solubility of hydroxides is easily determined through a titration with a suitable acid (such as HCl). From the molar solubility, the solubility equilibrium constant, K_{sp}, can be calculated and from this the ΔG° for the dissolution of the material can be determined. Using ΔG° values at two different temperatures and noting that the values of ΔH° and ΔS° are relatively invariant over small temperature ranges, the enthalpy and entropy changes can also be estimated. With knowledge of these constants, ΔG° and K_{sp} can be calculated at any temperature between 0 ˚C and 100 ˚C.

THE REACTION:

The solubility of an ionic substance in a solvent can be thought of as a reaction where the solid dissociates into ions in solution. In this experiment, the solubility of calcium hydroxide will be determined, as suggested in the reaction shown below.

$$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2\ OH^{-}{}_{(aq)}$$

Once equilibrium has been established and the solid removed, the concentration of hydroxide can be easily determined via an acid/base titration. Hydrochloric acid will be used to find the concentration of $OH^{-}{}_{(aq)}$.

$$HCl_{(aq)} + OH^{-}{}_{(aq)} \rightarrow H_2O_{(l)} + Cl^{-(aq)}$$

Note that the molar solubility of $Ca(OH)_2$ is *half* of the OH^- concentration found by titration.

Determination of K_{sp}, ΔG°, ΔH° and ΔS°

The concentration of hydroxide ion in a saturated solution of $Ca(OH)_2$ is found by titration with standardized hydrochloric acid. Since HCl is a strong acid and H^+ and OH^- react with 1:1 stoichiometry, we can use:

$$M_{HCl}V_{HCl} = M_{OH-}V_{OH-}$$

where M_{HCl} and M_{OH-} are the molarities and V_{HCl} and V_{OH-} are the volumes of the acid and hydroxide solutions, respectively. The *molar solubility* of the salt is equal to half of the hydroxide ion concentration

The **equilibrium constant**, $\mathbf{K_{sp}}$, for $Ca(OH)_2$ is:

$$\mathbf{K_{sp} = [Ca^{2+}][OH^-]^2}$$

Remember that the calcium ion concentration is half the hydroxide ion concentration determined by the titration.

The **Gibbs Free Energy**, $\mathbf{\Delta G^\circ}$, is related to the equilibrium constant (K_{sp}) by

$$\mathbf{\Delta G^\circ = -RT \ln K_{sp}}$$

where **R** is the **ideal gas constant** (R = 8.3145 J/mol-K) and **T** is the **absolute temperature** in Kelvin.

To find the **enthalpy** (ΔH°) and **entropy** (ΔS°) changes, the following equation is used

$$\mathbf{\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ}$$

where **T** is the absolute temperature. We assume that ΔH° and ΔS° do not change significantly with temperature which is usually true for this small of a temperature change. Using the free energies (ΔG°) found for two different temperatures, ΔH° and ΔS° values are found by solving for two unknowns in two equations.

Example:

Consider the solubility of $Sr(OH)_2$. Two solutions of $Sr(OH)_2$ are allowed to equilibrate, one at 0 ˚C and the other at 25 ˚C. A 10.00 mL aliquot of each solution is titrated with 0.2000 M HCl. 3.37 mL of the acid are required for the 0 ˚C solution, and 62.90 mL are required for the 25 ˚C solution.

At 0 ˚C, the $[OH^-]$ is found using:

$$\mathbf{[OH^-]} = ([HCl] * V_{HCl})/V_{OH^-} = (0.2000\text{ M} * 3.37\text{ mL})/10.00\text{ mL} = \mathbf{0.0674\ M}$$

Thus, the **molar solubility** of $Sr(OH)_2$ at 0 ˚C is 0.0674/2 = **0.0337 M**. K_{sp} at 0 ˚C can then be found:

$$\mathbf{K_{sp}} = [Sr^{2+}][OH^-]^2 = [0.0337][0.0674]^2 = \mathbf{1.53*10^{-4}}$$

ΔG° can be determined at 0 ˚C (273 K):

$$\mathbf{\Delta G^\circ} = -RT \ln K_{sp} = -(8.3145)(273) \ln(1.53*10^{-4}) = \mathbf{19.9\ kJ/mol}$$

Similarly, the molar solubility at 25 ˚C is found to be 0.6290 M; K_{sp} is 0.995; and ΔG° is 0.0124 kJ/mole.

Now we can determine ΔH° and ΔS° using the values of ΔG° at two temperatures:

$$\Delta G^\circ = 19.9\text{ kJ/mole} = \Delta H^\circ - (273 * \Delta S^\circ)$$
$$\Delta G^\circ = 0.0124\text{ kJ/mole} = \Delta H^\circ - (298 * \Delta S^\circ)$$

Subtracting the second equation from the first provides

$$19.9\text{ kJ/mol} - 0.0124\text{ kJ/mol} = \Delta H^\circ - \Delta H^\circ - (273 * \Delta S^\circ) + (298 * \Delta S^\circ)$$
$$19.9\text{ kJ/mole} = 25\ \Delta S^\circ$$

so ΔS° = 0.80 kJ/mole-K. Using this value of ΔS° at either temperature gives ΔH° = 240 kJ/mole.

PROCEDURE:

1. Begin preparing a 100 ˚C saturated calcium hydroxide solution by bringing 100 mL of deionized water to a boil in a 250 mL beaker (you will use this in Step 3.) **Record** the concentration of the standardized HCl provided in the laboratory. Obtain about **40 mL** of this HCl solution and place it in a 25 mL buret. (If you take more than 50 mL of HCl, a point penalty will be applied!!!)

2. A solution of calcium hydroxide will be stirring at room temperature in the laboratory. Draw off approximately 40 mL of this solution and **record the temperature**. **Filter** the solution using a long stem funnel until you have at least 30 mL of filtrate (if the filtering is slow, consider starting step 3 below.) Place 10.0 mL of the filtrate into a clean 125 mL Erlenmeyer flask and add 25 mL of deionized water and a few drops of bromothymol blue indicator. **Titrate** with the standard HCl solution until the **yellow** endpoint appears (probably no more than 5 mL of HCl will be required to reach the endpoint). Record the volume of HCl used to 0.01 mL. **Repeat** this procedure two more times.

3. If the roughly 100 mL of water has been boiling for a minute or two, then add about 2 g of $Ca(OH)_2$ to the water and keep it near boiling with occasional stirring as needed.

4. Bring your hot solution to a gentle boil for about two minutes, turn off the burner, **measure the temperature** (it should be close to boiling) and quickly draw off about 40 - 50 mL of solution. Quickly filter the solution using a clean, dry long stem funnel.

5. Place 10.0 mL of the cooled filtrate into each of three clean 125 mL Erlenmeyer flasks and add 25 mL of deionized water and a few drops of bromothymol blue indicator. When the solution is cool, titrate with the standard HCl solution until the **yellow** endpoint appears (probably no more than 5 mL of HCl will be required to reach the endpoint). Record the volume of HCl used to 0.01 mL. **Repeat** two more times.

6. Dispose of all used and excess chemicals in a waste container. Rinse your buret and all glassware with water before returning to its original location.

CALCULATIONS: *Be sure to look at the example on the previous page for hints on how to get started!*

1. Find the **average solubility** (and **parts per thousand**) of calcium hydroxide at each temperature by finding the hydroxide ion concentration and then converting this value to the molar solubility of $Ca(OH)_2$. If one of the three equivalence point volumes differs from the other two, it is acceptable to omit the differing value and use the two values with close precision.

2. Find $\mathbf{K_{sp}}$ at each temperature using the average solubility value. Find $\mathbf{\Delta G^\circ}$ at each temperature using the two values of K_{sp}.

3. Find $\mathbf{\Delta H^\circ}$ and $\mathbf{\Delta S^\circ}$ using the values of K_{sp} and ΔG° at the two temperatures.

Determination of K_{sp}, ΔG°, ΔH° and ΔS° for $Ca(OH)_2$ - *Worksheet*

Your name: **Lab Partner(s):**

Purpose: The goal of this lab is to find K_{sp}, ΔG°, ΔH° and ΔS° for $Ca(OH)_2$.

Goal #1: **Data**

Concentration of HCl (M): ____________________________

Temperature for first set of data = _______________°C *Lower temperature*

Temperature for second set of data = _______________°C *Higher Temperature*

mL HCl titrated at lower Temperature	mL HCl titrated at higher Temperature
_______________	_______________
_______________	_______________
_______________	_______________

Notes: (optional)

Goal #2: **Determine the solubility of $Ca(OH)_2$ at two different temperatures.** *We will do two simultaneous calculations in order to find the solubility of $Ca(OH)_2$ at each temperature. We can use the mL of HCl titrated and the molarity to find moles of HCl, and this equals moles of hydroxide (1:1 ratio). There are two hydroxides per one $Ca(OH)_2$, so we will apply this stoichiometry to find the moles of $Ca(OH)_2$ in the original mixture. Dividing by the liters of $Ca(OH)_2$ used (0.0100 L in this lab) will give us the solubility. This calculation scheme will be applied to both temperature sets in order to find the solubility at each temperature.*

Convert mL of HCl into moles of [OH^{-1}] at each temperature:

Convert mL to L of HCl
*Multiply L of HCl by (HCl molarity) * (1 mol OH^{-1} / 1 mol HCl) = this equals moles OH^{-1}*
*moles OH^{-1} * (1 mol $Ca(OH)_2$ / 2 moles OH^{-1}) / 0.0100 L = solubility of $Ca(OH)_2$ (in M)*

Concentration HCl (M): ___________________________ *from Goal #1*

At **lower** temperature:

Temperature = ____________ **°C** *from Goal #1*

_______ mL HCl equates to a solubility of ___________________ M

_______ mL HCl equates to a solubility of ___________________ M

_______ mL HCl equates to a solubility of ___________________ M

Average of three lower temperature solubilities = __________________

Parts per thousand = ______________________

Info on parts per thousand: **https://mhchem.org/ppt**

Show examples of how this work was accomplished

Goal #2: *(continued)*

At **higher** temperature:

Temperature = ____________ **°C** *from Goal #1*

_______ mL HCl equates to a solubility of ___________________ M

_______ mL HCl equates to a solubility of ___________________ M

_______ mL HCl equates to a solubility of ___________________ M

Average of three higher temperature solubilities = __________________

Parts per thousand = ______________________

Info on parts per thousand: **https://mhchem.org/ppt**

Show examples of how this work was accomplished

Goal #3: **Find the value of K_{sp} and ΔG° at each temperature.** *We can use K_{sp} = 4(solubility)^3 to convert each average solubility into a K_{sp} value. Using K_{sp}, we can convert each value into a ΔG° using the relation ΔG° = -RT ln K_{sp} where* ***R = 8.3145*** *J/mol*K and* ***T*** *=* ***Kelvin*** *temperature*

At **lower** temperature:

Lower temperature (°C) = _________ *from Goal #1*

Lower temperature (K) = _________

Average of three lower temperature solubilities = _____________ *from Goal #2*

K_{sp} = 4(*solubility*)^3 = _____________ *where solubility = average lower temp. solubility*

ΔG° = -RT ln K_{sp} = ______________________ (kJ/mol)

*Use R = 8.3145 J/mol*K, T = Kelvin temp., Ksp = answer on previous line*
Convert J to kJ to get the final answer

Show examples of how this work was accomplished

Goal #3: *Continued*

At **higher** temperature:

Higher temperature (°C) = _________ *from Goal #1*

Higher temperature (K) = _________

Average of three higher temperature solubilities = _____________ *from Goal #2*

$\boldsymbol{K}_{\mathbf{sp}} = 4(\textit{solubility})^3 =$ ____________ *where solubility = average high temp. solubility*

$\Delta\mathbf{G}^\circ = -RT \ln K_{sp} =$ _____________________ (kJ/mol)

*Use R = 8.3145 J/mol*K, T = Kelvin temp., Ksp = answer on previous line*
Convert J to kJ to get the final answer

Show examples of how this work was accomplished

Goal #4: **Use the values of ΔG° and T to find ΔH° and ΔS°.** *We will use the ΔG° and Kelvin temperatures to find ΔH° and ΔS° using the Gibbs Equation, $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$*

From Goal #3:

Lower temperature (K) = _________ ΔG° = ______________ (kJ/mol)

Higher temperature (K) = _________ ΔG° = ______________ (kJ/mol)

Find ΔH° and ΔS° in the space below. *Clearly show your work for full credit.*

ΔH° = ______________ (kJ/mol) ΔS° = ______________ (kJ/mol*K)

Postlab Questions:

1. A 10.00 mL sample of $Ba(OH)_2$ at 0. ˚C is titrated with 0.2500 M HCl, and 4.80 mL of the acid are used to reach the yellow endpoint.

   a. Calculate the concentration of hydroxide in the $Ba(OH)_2$ solution.

   b. Determine the molar solubility and K_{sp} of $Ba(OH)_2$.

   c. Calculate ΔG° for this reaction using the value of K_{sp}.

2. A second 10.00 mL sample of $Ba(OH)_2$ is obtained at a temperature of 50. ˚C. This solution is titrated with 44.15 mL of 0.2500 M HCl to reach the yellow endpoint.

   a. Calculate the concentration of hydroxide in this $Ba(OH)_2$ solution.

   b. Determine the molar solubility and K_{sp}.

   c. Calculate ΔG° for this reaction using the value of K_{sp}.

3. Using the values of ΔG° at 0. ˚C and 50. ˚C, calculate ΔH° and ΔS° for this reaction.

<u>Postlab Questions</u>: *Continued*

4. Look up and report the value of K_{sp} for calcium hydroxide at 25 ˚C in your textbook or on the internet. How does your room temperature ("lower temperature") value compare to the reference? What are the sources of error? Cite your reference for the K_{sp} value.

5. Calculate the molar solubility of $Ca(OH)_2$ at 50 ˚C using your experimental values of ΔH° and ΔS°. (*Hint:* First find ΔG° at the new temperature, then determine Ksp and finally solubility.) Is this solubility the average of the 0 ˚C and 100 ˚C solubilities? Why or why not? (*Hint:* are the equations used to determine solubility linear?)

CH 223 Spring 2025:
"Qualitative Analysis of Group I Cations" *(in class)* ***Lab:*** *Instructions*

Note: **This is the lab for section 01 and H1 of CH 223 only.**

- *If you are taking section W1 of CH 223*, please use this link:
  http://mhchem.org/q/8b.htm

Step One:

Get a printed copy of this lab! You will need a printed (hard copy) version of pages Ia-8-2 through Ia-8-7 to complete this lab. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.

Step Two:

Bring the printed copy of the lab with you on Monday, May 19 (section 01) *or* **Wednesday, May 21 (section H1.)** During lab in room AC 2507, you will use these sheets (with the valuable instructions!) to gather data, all of which will be recorded in the printed pages below.

Step Three:

Complete the lab work and calculations on your own, then **turn it in** (page Ia-8-7 *only* to avoid a point penalty) **to the instructor on Wednesday, May 29 at 9 AM in AC 1303 (section 01)** *or* **Wednesday, May 29 at 1:10 PM in AC 2501 (section H1.)**

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

Qualitative Analysis Of Group I Cations

In previous labs you have determined the amount of an unknown species present, such as percent chloride, identification of an unknown copper, and the molarity of various acid and base solutions. These experiments are a part of chemistry called *quantitative analysis*. When a chemist performs a **qualitative** analysis of a sample, s/he is more interested in the nature of the species present in a sample rather than the amount.

A set of experiments can be performed on an unknown mixture to precipitate cations in a sequential order. Under specific conditions, if a precipitate contains only one cation, the presence of that cation can be determined. Various types of reactions can be performed to separate the ions, including acid-base, complex ion formation, redox and other precipitation reactions. Ultimately, the sample should be resolved into fractions each containing one cation, whose presence is established by the formation of a characteristic precipitate or colored complex ion. The first step is to develop a scheme for the separation and identification of the cations.

Cations are typically divided into **Groups**, where each group shares a common reagent that can be used for selective precipitation. The classic qualitative analysis scheme used to separate various groups of cations is shown in the flow chart on the next page.

Over the next several weeks, you will study group I and III cations. You will develop a scheme to determine the cations present in an unknown mixture. Finally, you will carry out this scheme.

Precipitation and Separation of Group I Cations:

Pb^{+2}, Hg_2^{+2}, and **Ag^+** are all insoluble in cold water. They can be removed as a group from solution by the addition of HCl via simple precipitation in the following net ionic reaction:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

It is important to add enough HCl to ensure complete precipitation, but not too large an excess. In highly concentrated HCl solutions, chloro-complexes may form such as $AgCl_2^{-1}$.

Lead chloride can be separated from AgCl and Hg_2Cl_2 by heating with water, essentially reversing the above reaction. Once Pb^{+2} is in solution, you can discern its presence by adding chromate ion to produce a **yellow** solid:

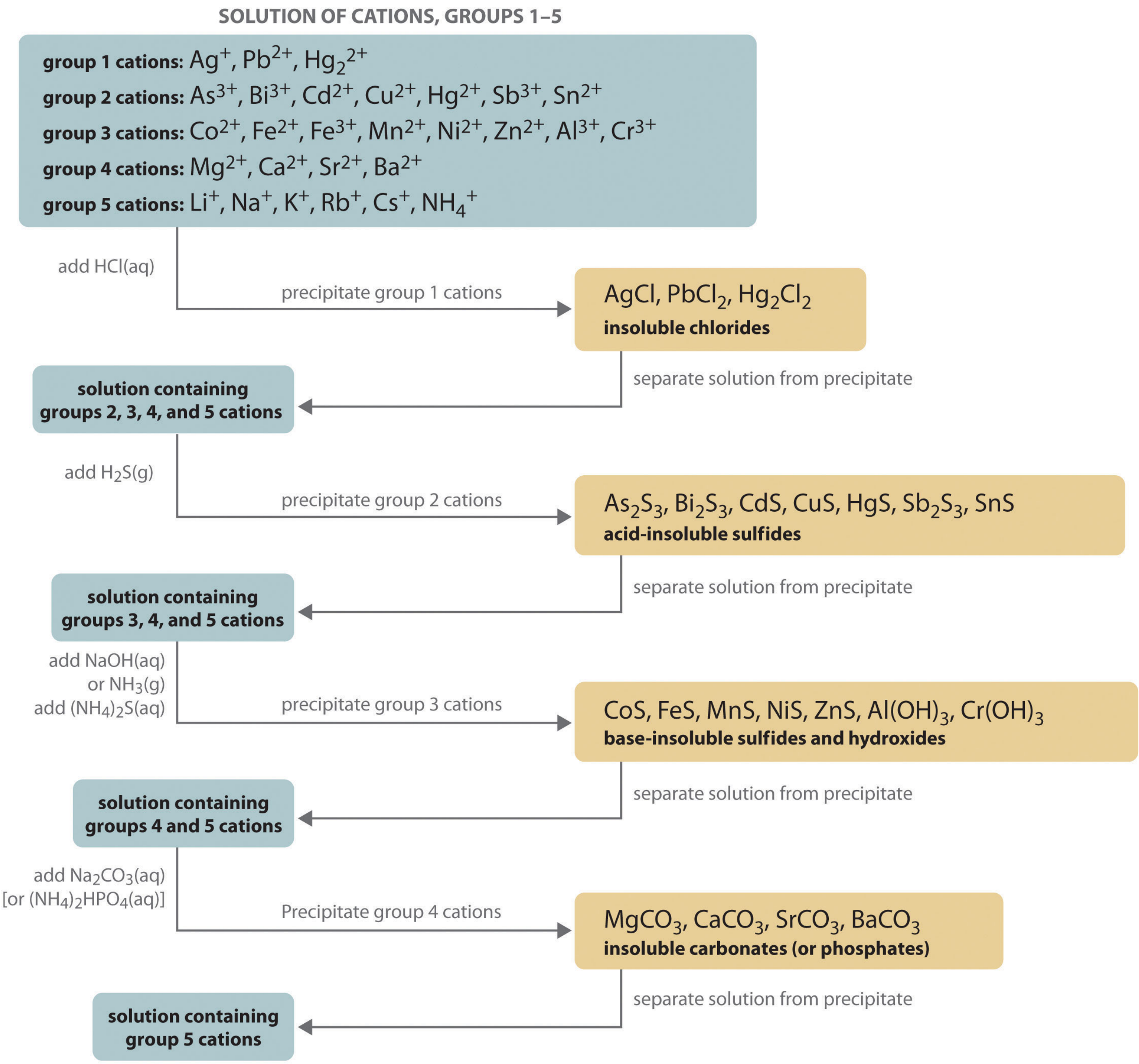
$$Pb^{+2}(aq) + CrO_4^{-2}(aq) \rightarrow PbCrO_4(\text{yellow solid})$$

Hg_2Cl_2 can be distinguished from AgCl by reaction with ammonia via oxidation reduction to yield finely divided black metallic mercury and a white complex compound $HgNH_2Cl$. As the reaction proceeds, the solid appears to change colors from white to **black** or **gray**:

$$Hg_2Cl_2(\text{white solid}) + 2\ NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq) + Hg(\text{black liquid}) + HgNH_2Cl(\text{white solid})$$

Silver chloride also reacts with aqueous ammonia to form a complex ion that remains in solution. Addition of a strong acid will destroy the complex and confirm the presence of silver ion by re-precipitating the **white** AgCl solid:

$$AgCl(s) + 2\ NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$$
$$Ag(NH_3)_2^+(aq) + 2\ H^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + 2\ NH_4^+(aq)$$



As you can see from the chart above, there are many Cation Groups.
We will analyze Group I Cations (the "Silver group") and some of the Group III Cations.

Laboratory Techniques: Above all else, **you *must* wear safety glasses at all times** while performing Qualitative Analysis labs! Failure to bring your own pair of safety glasses will result in a point penalty. Glasses must be worn over prescription glasses on these labs.

Attire in the Lab:
Please do not wear open toed shoes or sandals; shorts and shirts that show mid-riff areas are disallowed. You will be sent home to change if proper attire is not worn, so please, think safe when dressing for lab!

Waste:
Make sure all waste is placed in a proper waste container - do not pour anything down the drain.

Cleanliness:
Make sure that all test tubes, stirring rods, etc. are clean. Rinse all equipment with water before and after use. Use clean droppers.

Centrifuging:
Use centrifuge tubes when centrifuging - do not use ordinary test tubes. A tube of approximately the same mass and volume in the opposite slot of the centrifuge must be used to balance the centrifuge. Generally centrifuging for a minute or less is sufficient for these labs.

Decanting:
After centrifuging, the **supernatant** (the liquid above a precipitate; it is also called the *decantate*) is usually **decanted** (poured) into a clean test tube with the intent of keeping the solid in the original container. Carefully tip the test tube and pour off the supernatant without disturbing the solid. It may be poured directly, or a stirring rod may be placed across the mouth of the test tube to direct the supernatant into a clean test tube.

Washing a Precipitate:
After separation from the supernatant, a precipitate is often washed to free it from reagents that might interfere at a later stage. Usually, the rinse is deionized water, but other liquids or solutions may be used. After thorough stirring, centrifuge the sample and decant the wash solution.

Heating:
Due to the small quantity of material being heated, solutions in test tubes can reach its boiling point within a few seconds, and chemicals may be ejected violently from the container. If the solution volume is too large to fit in a centrifuge tube, reducing the volume can be accomplished by placing the solution in a 30 mL beaker and placing it on the hot plate. ***Watch the solution on the hot plate intently*** - if overheated, you may be left with a crusty remnant which is hard to reconstitute. Using a water bath is safer, but slower.

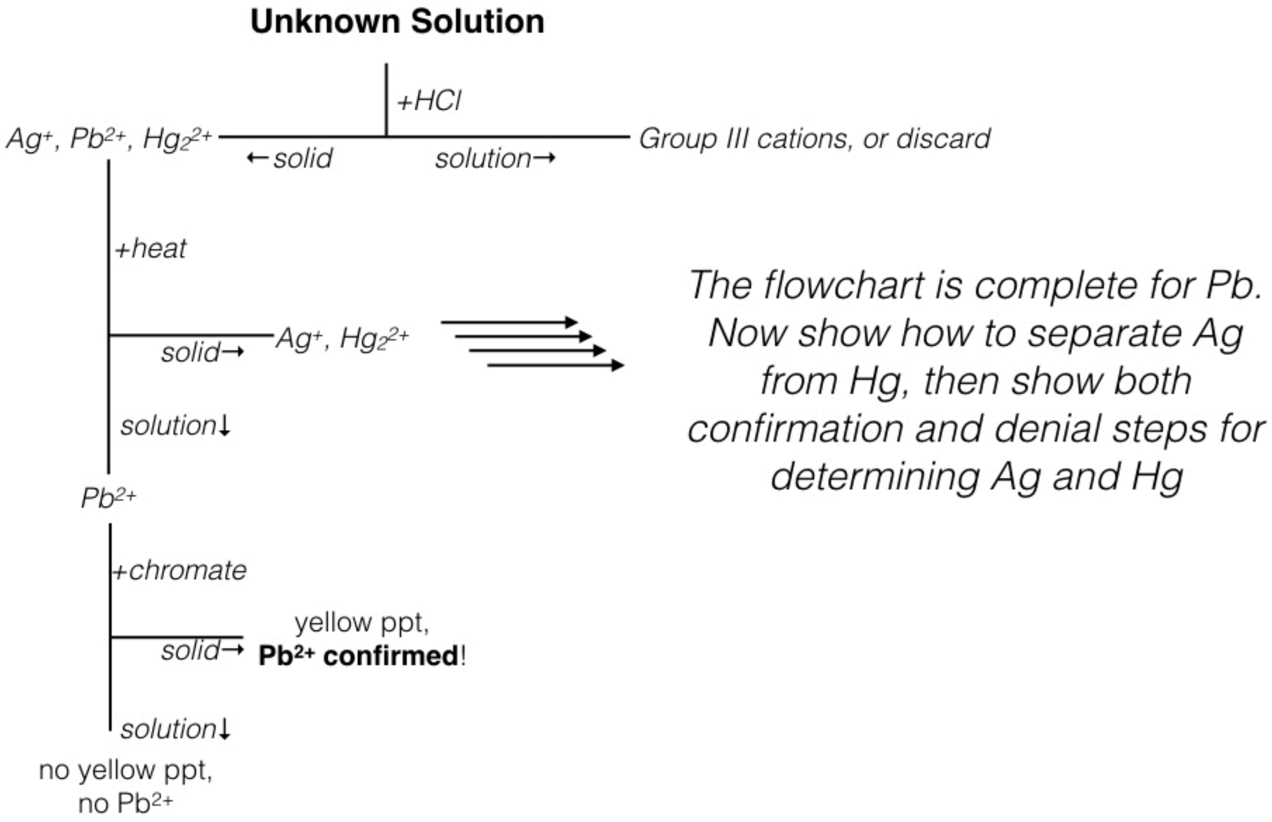
Testing pH:
When directed to check the pH of a solution, stir the solution thoroughly with a clean glass stirring rod and then touch the tip of the rod to a piece of litmus paper. Several such tests may be performed on each strip of paper. Red litmus paper will turn blue in basic solutions; blue litmus paper will turn red in acidic solutions.

Flow Charts:

It is possible to summarize the directions for the analysis of the Group I cations in a flow chart. In a flowchart, successive steps in the procedure are linked with arrows or lines. Reactant cations are at one end of the line; reagents and conditions used to carry out each step are placed alongside the lines. The line splits to show the two possible outcomes (yellow ppt = Pb^{+2} present; no ppt = absence). A flow chart for the separation of Group I cations should be included in your lab report.

A *partially* completed flowchart for the Group I Cations lab is included below. When you complete a flowchart, make sure that it shows clearly where each cation is separated out; also show the confirmation of each cation (with both yes and no options to indicate the presence or absence of the cation.)

Flowcharts may be completed on paper by hand or electronically on the computer; the choice is yours.



The flowchart is complete for Pb. Now show how to separate Ag from Hg, then show both confirmation and denial steps for determining Ag and Hg

PROCEDURE: *All waste must go in a waste bottle. Safety glasses are mandatory for everyone; no open toed shoes or sandals, no shorts or mid-riff showing shirts.*

Step 1: Preparation:

Prepare a 1 mL "**known**" **sample** by placing 7 drops of each of the following into a centrifuge tube: 0.1 M $AgNO_3$, 0.3 M $Pb(NO_3)_2$ and 0.1 M $Hg_2(NO_3)_2$. Prepare a second 1 mL "**unknown**" **sample** using 1 mL of your unknown liquid. Be sure to write the identity of your unknown. Your unknown will have between one and three of the Group I cations in it, and the known will act as a "control" to see appropriate color changes, etc. throughout the tests.

You will perform the following tests upon *each* solution (both the known and unknown solutions) simultaneously. Be sure to write down any color changes, precipitates, etc. that you might observe in your lab notebook.

Step 2: Precipitation of Group I Cations:

Add two drops of 6 M HCl and mix with a clean stirring rod. Centrifuge the mixture being certain a centrifuge tube of equal volume is placed opposite your centrifuge tube as a balance. Add one more drop of 6 M HCl to the test tube to be certain of complete precipitation. Centrifuge again if necessary. Decant the supernatant into another test tube and save for later analysis for Group III cations (if appropriate, i.e. on the Final Lab). The precipitate should be white and contain the chlorides of the Group I cations.

Step 3: Separation and ID of Lead:

Rinse the precipitate from Step 2 with 1-2 mL of deionized water. Stir, centrifuge and discard the liquid. Add 2 mL deionized water and place in boiling water for two minutes, stirring occasionally to dissolve most of the $PbCl_2$. Centrifuge and decant the liquid into another test tube. Save the precipitate for later tests for silver and mercury.

Add one drop of 6 M acetic acid and two drops of 1 M K_2CrO_4 to the liquid. A bright yellow precipitate will appear if the lead (II) ion is present.

Step 4: Separation and ID of Mercury:

To the precipitate from step 3, add 1 mL 6 M NH_3 and stir. Centrifuge and decant the liquid into a test tube for testing for Ag^+ (Step 5.) A gray or black precipitate confirms the presence of the mercury(I) ion.

Step 5: Identification of Silver:

Add 6 M HNO_3 to the liquid from step 4 until it is acidic to litmus. Test for acidity by touching the end of your stir rod to litmus paper. If Ag^+ is present, it will precipitate in the acidified solution as white AgCl.

Step 6: Cleanup!

Please rinse all glassware and equipment prior to leaving lab. Return cleaned centrifuge tubes to the container without masking tape.

Include answers to the following postlab questions (most of which can be found on the introductory page for this lab, hint, hint ☺).

Qualitative Analysis of Group I Cations Lab - *Worksheet*

YOUR NAME: ________________________ ***LAB PARTNER(s):*** __________________

Unknown Number: ___________

Circle *either* yes or no for each metal cation in your unknown.

Pb^{2+}: yes no

Hg_2^{2+}: yes no

Ag^+: yes no

Include a flowchart showing the overall steps used to separate the Group I cations with your lab report.

Postlab Questions:

1. Write balanced net ionic equations for the following reactions:
    a. The precipitation reaction of the chloride of Hg_2^{+2} in step 2.

    b. The formation of the yellow precipitate in step 3.

    c. The formation of the black precipitate in step 4.

    d. The reaction that occurs in step 5.

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CH 223 Spring 2025: **"Qualitative Analysis of Group III Cations"** *(in class)* ***Lab:*** *Instructions*

Note: **This is the lab for section 01 and H1 of CH 223 only.**

- *If you are taking section W1 of CH 223*, please use this link:
  http://mhchem.org/q/9b.htm

Step One:

Get a printed copy of this lab! You will need a printed (hard copy) version of pages Ia-9-2 through Ia-9-5 to complete this lab. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.

Step Two:

Bring the printed copy of the lab with you on Monday, June 2 (section 01) *or* **Wednesday, June 4 (section H1).** During lab in room AC 2507, you will use these sheets (with the valuable instructions!) to gather data, all of which will be recorded in the printed pages below.

Step Three:

Complete the lab work, then **turn it in** (page Ia-9-5 *only* to avoid a point penalty) **at the *END OF LAB* to the instructor on Monday, June 2 (section 01)** *or* **Wednesday, June 4 (section H1.)**

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

Qualitative Analysis Of Group III Cations

The four group III cations in this lab are **Cr^{+3}**, **Al^{+3}**, **Fe^{+3}**, and **Ni^{+2}**. The first step in analysis involves separating the ions into two subgroups by treating the solution with NaOH and NaOCl. The hypochlorite ion oxidizes Cr(III) to a higher, more stable oxidation state (namely Cr(VI)) which is soluble:

$$2\ Cr^{+3}(aq) + 3\ OCl^{-1}(aq) + 10\ OH^{-1}(aq) \rightarrow 2\ CrO_4^{-2}(aq) + 3\ Cl^{-1}(aq) + 5\ H_2O(l)$$

In addition, Al^{+3} forms a soluble hydroxo-complex ion in the presence of excess hydroxide:

$$Al^{+3}(aq) + 4\ OH^{-1}(aq) \rightarrow Al(OH)_4^{-1}(aq)$$

In contrast, Ni^{+2} and Fe^{+3} do not readily form hydroxo-complexes and are not oxidized by hypochlorite. They form insoluble hydroxides under these conditions:

$$Ni^{+2}(aq) + 2\ OH^{-1}(aq) \rightarrow Ni(OH)_2(\text{green solid})$$

$$Fe^{+3}(aq) + 3\ OH^{-1}(aq) \rightarrow Fe(OH)_3(\text{red solid})$$

To separate aluminum from chromium, the solution containing CrO_4^{-2} and $Al(OH)_4^-$ is acidified to destroy the hydroxo-complex:

$$Al(OH)_4^{-1}(aq) + 4\ H^+(aq) \rightarrow Al^{+3}(aq) + 4\ H_2O(l)$$

Treatment with aqueous ammonia gives a gelatinous **white** precipitate of aluminum hydroxide. The concentration of hydroxide in ammonia is too low to form the hydroxo-complex:

$$Al^{+3}(aq) + 3\ NH_3(aq) + 3\ H_2O(l) \rightarrow 3\ NH_4^+(aq) + Al(OH)_3(\text{white solid})$$

The chromate ion remains in solution. It can be tested and confirmed by precipitation as yellow $BaCrO_4$:

$$Ba^{+2}(aq) + CrO_4^{-2}(aq) \rightarrow BaCrO_4(\text{yellow solid})$$

The $BaCrO_4$ precipitate dissolves in acid. The solution is then treated with H_2O_2 to produce a **deep blue** color due to the presence of a peroxo-compound, probably CrO_5:

$$2\ BaCrO_4(s) + 4\ H^+(aq) + 4\ H_2O_2(aq) \rightarrow 2\ Ba^{+2}(aq) + 6\ H_2O(l) + 2\ CrO_5(\text{blue, aq})$$

The mixed precipitate of $Ni(OH)_2$ and $Fe(OH)_3$ can be dissolved by adding a strong acid. The Ni^{+2} and Fe^{+3} ions can be separated by adding ammonia. Ni^{+2} is converted to the deep-blue complex $Ni(NH_3)_6^{+2}$ which stays in solution. The Fe^{+3} ion does not readily form a complex and re-precipitates as $Fe(OH)_3$:

$$Ni^{+2}(aq) + 6\ NH_3(aq) \rightarrow Ni(NH_3)_6^{+2}(\text{blue, aq})$$

$$Fe^{+3}(aq) + 3\ NH_3(aq) + 3\ H_2O(l) \rightarrow 3\ NH_4^+(aq) + Fe(OH)_3(\text{red solid})$$

Confirm the presence of Ni^{+2} by adding dimethylglyoxime (DMG), $C_4H_8N_2O_2$, to give a **deep rose** precipitate:

$$Ni^{+2}(aq) + 2\ C_4H_8N_2O_2(aq) \rightarrow 2\ H^+(aq) + Ni(C_4H_7N_2O_2)_2(\text{red solid})$$

Confirm the presence of Fe^{+3} by dissolving $Fe(OH)_3$ in a strong acid and adding KSCN to form a **blood-red** $FeSCN^{+2}$ complex ion:

$$Fe^{+3}(aq) + SCN^-(aq) \rightarrow FeSCN^{+2}(\text{red, aq})$$

<u>PROCEDURE</u>: ***Safety glasses required for everyone****, all the time - no open toed shoes or sandals, no shorts or mid-riff showing shirts.* ***This can be a longer lab****, so come prepared and organized to maximize your lab experience.*

Step 1: Preparation: If you are working on the analysis of only group III ions, prepare a known solution by mixing 5-6 drops each of 0.1 M solutions of Fe^{+3}, Al^{+3}, Cr^{+3}, and Ni^{+2} in a 30 mL beaker. Also obtain an unknown to analyze at the same time for the presence of group III cations and use about 20-24 drops in your analysis.

Step 2: Oxidation of Cr(III) to Cr(VI) and Separation of Insoluble Hydroxides: Add 1 mL of 6 M NaOH to the solution in a 30 mL beaker. Boil very gently for 1 minute while stirring. Remove heat and slowly add dropwise 1 mL of 1 M NaClO. Swirl the beaker for 30 seconds, using tongs if necessary. Boil the mixture for 1 minute. Centrifuge. Transfer the supernatant (which contains the aluminum and chromate) to a separate tube. Wash the precipitate (which contains iron and nickel hydroxides) with 2 mL water and 0.5 mL of 6 M NaOH: stir, centrifuge, decant and discard the wash. Add 1 mL of water and 1 mL of 6 M HNO_3 to the solid and put it aside until step 6.

Step 3: Separation of Al from Cr: Acidify the solution from step 2 by adding 6 M acetic acid in **2.0 mL increments** until, after stirring, the mixture is definitely acidic to litmus (it might take up to 30 mL or more.) If necessary, transfer the solution to a 30 mL beaker and boil it to reduce its volume to about 3 mL. Pour the solution into a test tube. Add 6 M NH_3 in 5 drop increments until the solution is basic to litmus; and then add 0.5 mL excess. Stir the mixture for one minute to bring the system to equilibrium. If aluminum is present, a light, translucent gelatinous white precipitate of $Al(OH)_3$ may be floating in the clear to yellow solution. Centrifuge and transfer the liquid (which contains CrO_4^{-2}) to another test tube.

Step 4: Confirmation of the Presence of Aluminum: Wash the precipitate from step 3 with 3 mL water, warming the test tube in the water bath and stirring well. Centrifuge and discard the wash. Dissolve the precipitate in 2 drops of 6 M CH_3CO_2H (no more, no less!). Add 3 mL of water and 1-2 drops of aluminon. Stir. If Al^{+3} is present, the solution will turn a lovely rose-pink color due to the presence of a very fine red or pink precipitate.

Step 5: Confirmation of the Presence of Chromium: A yellow liquid from step 3 *suggests* but does not confirm the presence of chromium. To the solution add 0.5 mL of 1.0 M $BaCl_2$. In the presence of chromium a finely divided yellow precipitate of $BaCrO_4$ appears. Put the test tube in boiling water for two minutes. Centrifuge and discard the liquid. Wash the solid with 2 mL of water, centrifuge and discard the wash. To the solid add 0.5 mL of 6 M HNO_3. Stir to dissolve $BaCrO_4$. Add 1 mL of water; stir the orange solution. Add 2 drops of 3% H_2O_2. A deep blue solution, which may fade rapidly, confirms the presence of chromium.

Step 6: Separation of Iron and Nickel: Returning to the precipitate from step 2, stir to dissolve the solid in the HNO_3. If necessary, warm the test tube in the water bath to completely dissolve the solid. Add 6 M NH_3 until the solution is basic to litmus. At this point, iron will precipitate as brown $Fe(OH)_3$. Add 1 mL more of the NH_3 and stir to bring the nickel into solution as the $Ni(NH_3)_6^{+2}$ ion. Centrifuge and decant the liquid into a test tube. Save the precipitate for step 8 to test for the presence of iron.

Step 7: Confirmation of the Presence of Nickel: If the solution from step 6 is blue, nickel may be present. To the solution add 0.5 mL dimethylglyoxime (DMG) reagent. Formation of a rose-red precipitate proves the presence of nickel.

Step 8: Confirmation of the Presence of Iron: Dissolve the precipitate from step 6 in 0.5 mL of 6 M HCl. Add 2 mL water and stir. Add 2 drops of 1.0 M KSCN. Iron is present if a deep red solution of $FeSCN^{+2}$ is formed.

Step 9: Cleanup! Please rinse all glassware and equipment prior to leaving lab. Return cleaned centrifuge tubes to the container without masking tape.

Make sure you include your unknown number or letter!

Answers to the postlab questions can mostly be found on the main page of this lab, hint, hint ☺.

Qualitative Analysis of Group III Cations Lab - *Worksheet*

YOUR NAME: ______________________ ***LAB PARTNER(s):*** _________________

Unknown Number: ___________

Circle *either* yes or no for each metal cation in your unknown.

Fe^{3+}:	yes	no
Ni^{2+}:	yes	no
Cr^{3+}:	yes	no
Al^{3+}:	yes	no

Postlab Questions:

1. Write balanced net ionic equations for the following reactions:
   a. Dissolving $Fe(OH)_3$ in nitric acid

   b. Oxidation of Cr(III) by hypochlorite ion in base.

   c. The confirmatory test for Ni^{+2}. (Step 7)

   d. The confirmatory test for Fe^{+3}. (Step 8)

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CH 223 Spring 2025:

Problem Set #1

Instructions

Step One (all sections):

- **Learn the material** for Problem Set #1 by **reading Chapter 13** of the textbook and/or by watching the videos found on our website (https://mhchem.org/223)
- **Try the problems** for Problem Set #1 found on the next pages on your own first. **Write out the answers (and show your work) by hand (on a tablet or paper)**; do not type your answers (and work) to avoid a point penalty. If you write the answers on the problem set itself, you will receive fewer points. Include your name on your problem set!

Step Two:

Section 01 and H1: We will go over Problem Set #1 during recitation. ***Self correct all problems*** of your problem set before turning it in at the end of recitation.

- *Section 01:* due **Monday, April 7 at 1:10 PM**
- *Section H1:* due **Wednesday, April 9 at 1:10 PM**

Section W1: **Watch the recitation video** for Problem Set #1:

http://mhchem.org/v/m.htm

- **Self correct *all* of the problems** while viewing the video. Mark correct problems with a star (or other similar mark), and correct all incorrect problems (show the correct answer and the steps required to achieve it.)
- **Submit Problem Set #1 via email (mike.russell@mhcc.edu) as a single PDF file** (use CamScanner (https://camscanner.com), CombinePDF (https://combinepdf.com), etc.) **by 11:59 PM Wednesday, April 9.**

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

CH 223 Problem Set #1

** Complete problem set on separate pieces of paper showing all work, circling final answers, etc.*
** Self correct your work before turning it in to the instructor.*

Covering: **Chapter Thirteen** *and* **Chapter Guide One**
Important Tables and/or Constants: **R = 0.082057 L atm mol^{-1} K^{-1}, 760 mm Hg = 1 atm**

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1. Write equilibrium constant expressions for the following reactions. For gases use either pressures or concentrations.
   a. $3\ O_2(g) \rightleftharpoons 2\ O_3(g)$
   b. $Fe(s) + 5\ CO(g) \rightleftharpoons Fe(CO)_5(g)$
   c. $(NH_4)_2CO_3(s) \rightleftharpoons 2\ NH_3(g) + CO_2(g) + H_2O(g)$
   d. $Ag_2SO_4(s) \rightleftharpoons 2\ Ag^+(aq) + SO_4^{2-}(aq)$
2. The equilibrium constant, *K*, for the reaction:
   $$2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$$
   is 3.9×10^{-3} at 300 °C. A mixture contains the gases at the following concentrations: [NOCl] = 5.0×10^{-3} M, [NO] = 2.5×10^{-3} M, and [Cl_2] = 2.0×10^{-3} M. Is the reaction at equilibrium at 300 °C? If not, in which direction does the reaction proceed to come to equilibrium?
3. An equilibrium mixture of SO_2, O_2 and SO_3 at 1000 K contains the gases at the following concentrations: [SO_2] = 3.77×10^{-3} M, [O_2] = 4.30×10^{-3} M, and [SO_3] = 4.13×10^{-3} M. Calculate the equilibrium constant, K_c, for the reaction:
   $$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$
4. You place 3.00 mol of pure SO_3 in an 8.00 L flask at 1150 K. At equilibrium, 0.58 mol of O_2 has formed. Calculate K_c for the reaction at 1150 K using the reaction:
   $$2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$$
5. Cyclohexane, C_6H_{12}, a hydrocarbon, can isomerize or change into methylcyclopentane, $C_5H_9CH_3$, a compound of the same formula but with a different molecular structure. The equilibrium constant has been estimated to be 0.12 at 25 °C. If you originally placed 0.045 mol of cyclohexane in a 2.8 L flask, what would be the concentrations of cyclohexane and methylcyclopentane when equilibrium is established? Use the equation:
   $$C_6H_{12}(g) \rightleftharpoons C_5H_9CH_3(g)$$
6. K_p for the following reaction is 0.16 at 25 °C:
   $2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$

   The enthalpy change for the reaction at standard conditions is +16.3 kJ. Predict the effect of the following changes on the position of the equilibrium; that is, state which way the equilibrium will shift (left, right, or no change) when each of the following changes is made.
   a. adding more $Br_2(g)$
   b. removing some NOBr(g)
   c. decreasing the temperature
   d. increasing the container volume

Problem Set #1 continues on the next page

7. The decomposition of NH_4HS is an endothermic process:
   $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
   a. Using Le Chatelier's principle, how would increasing the temperature affect the equilibrium?
   b. How would K be affected if additional NH_3 is placed in the flask?
   c. What will happen to the pressure of NH_3 if some H_2S is removed from the flask?
8. The equilibrium constant for the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

   is 1.7×10^{-3} at 2300 K.
   a. What is *K* for the reaction when written as follows:

$$\tfrac{1}{2}\,N_2(g) + \tfrac{1}{2}\,O_2(g) \rightleftharpoons NO(g)$$

   b. What is *K* for the following reaction?

$$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

9. The equilibrium constant *K* for the reaction

$$CO_2(g) \rightleftharpoons CO(g) + \tfrac{1}{2}\,O_2(g)$$

   is 6.66×10^{-12} at 1000 K. Calculate *K* for the reaction

$$2\,CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g)$$

10. Ammonium iodide dissociates reversibly to ammonia and hydrogen iodide if the salt is heated to a sufficiently high temperature. Some ammonium iodide is placed in a flask, which is then heated to 400 °C. If the total pressure in the flask when equilibrium has been achieved is 705 mm Hg, what is the value of K_p (when partial pressures are in atmospheres)?

$$NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$$

11. In the gas phase, acetic acid exists as an equilibrium of monomer and dimer molecules. The dimer consists of two molecules of acetic acid linked through hydrogen bonds. The equilibrium constant, *K*, for the monomer-dimer equilibrium shown below has been determined to be 3.2×10^4. Assume that acetic acid is present initially at a concentration of 5.4×10^{-4} M at 25 °C and that no dimer is present initially.

$$2\,CH_3CO_2H(g) \rightleftharpoons (CH_3CO_2H)_2(g)$$

   a. What percentage of the acetic acid is converted to the dimer?
   b. As the temperature increases, in which direction does the equilibrium shift? (Recall that hydrogen bond formation is an exothermic process.)
12. At 450 °C, 3.60 mol of ammonia is placed in a 2.00 L flask and allowed to decompose into the elements. If the experimental value of K_c is 6.3 for this reaction at this temperature, calculate the equilibrium concentration of each reagent. What is the total pressure in the flask? The reaction:

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$$

Problem Set #1 continues on the next page

13. K_c for the decomposition of ammonium hydrogen sulfide is 1.8 x 10^{-4} at 25 °C. The reaction:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

   a. When the pure salt decomposes in a flask, what are the equilibrium concentrations of NH_3 and H_2S?
   b. If NH_4HS is placed in a flask already containing 0.020 M of NH_3 and then the system is allowed to come to equilibrium, what are the equilibrium concentrations of NH_3 and H_2S?

14. The dissociation of calcium carbonate has an equilibrium constant K_p = 1.16 at 800. °C.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

   a. What is K_c for the reaction?
   b. If you place 22.5 g of $CaCO_3$ in a 9.56 L container at 800. °C, what is the pressure of CO_2 in the container?
   c. What percentage of the original 22.5 g sample of $CaCO_3$ remains undecomposed at equilibrium?

CH 223 Spring 2025:

Problem Set #2

Instructions

Step One (all sections):

- **Learn the material** for Problem Set #2 by **reading Chapter 14 (up to 14.5) and Chapter 15 (15.2)** of the textbook and/or by watching the videos found on our website (https://mhchem.org/223)
- **Try the problems** for Problem Set #2 found on the next pages on your own first. **Write out the answers (and show your work) by hand (on a tablet or paper)**; do not type your answers (and work) to avoid a point penalty. If you write the answers on the problem set itself, you will receive fewer points. Include your name on your problem set!

Step Two:

Section 01 and H1: We will go over Problem Set #2 during recitation. ***Self correct all problems*** of your problem set before turning it in at the end of recitation.

- *Section 01:* due **Monday, April 14 at 1:10 PM**
- *Section H1:* due **Wednesday, April 16 at 1:10 PM**

Section W1: **Watch the recitation video** for Problem Set #2:

http://mhchem.org/v/n.htm

- **Self correct *all* of the problems** while viewing the video. Mark correct problems with a star (or other similar mark), and correct all incorrect problems (show the correct answer and the steps required to achieve it.)
- **Submit Problem Set #2 via email (mike.russell@mhcc.edu) as a single PDF file** (use CamScanner (https://camscanner.com), CombinePDF (https://combinepdf.com), etc.) **by 11:59 PM Wednesday, April 16.**

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

CH 223 Problem Set #2

** Complete problem set on separate pieces of paper showing all work, circling final answers, etc.*
** Self correct your work before turning it in to the instructor.*

Covering: **Chapter Fourteen Part I** *and* **Chapter Guide Two**
Important Tables and/or Constants: The **Table of Acids and Bases for CH 223** *which follows this problem set, and* **K_w = 1.00 x 10^{-14}** at 25 °C

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1. In each of the following acid-base reactions, identify the Brønsted acid and base on the left and their conjugate partners on the right.
   a. $HCO_2H(aq) + H_2O(\ell) \rightleftharpoons HCO_2^{-1}(aq) + H_3O^+(aq)$
   b. $NH_3(aq) + H_2S(aq) \rightleftharpoons NH_4^+(aq) + HS^{-1}(aq)$
   c. $HSO_4^{-1}(aq) + OH^{-1}(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(\ell)$
2. What are the products of each of the following acid-base reactions? Indicate the acid and its conjugate base, and the base and its conjugate acid.
   a. $HClO_4 + H_2O \rightarrow$
   b. $NH_4^+ + H_2O \rightarrow$
3. Write balanced equations showing how the HPO_4^{2-} ion of sodium hydrogen phosphate, Na_2HPO_4, can be a Brønsted acid or a Brønsted base.
4. Several acids are listed here with their respective equilibrium constants:

$$HF(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + F^{-1}(aq)$$
$$K_a = 7.2 \times 10^{-4}$$
$$HPO_4^{-2}(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + PO_4^{-3}(aq)$$
$$K_a = 3.6 \times 10^{-13}$$
$$CH_3CO_2H(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^{-1}(aq)$$
$$K_a = 1.8 \times 10^{-5}$$

   a. Which is the strongest acid? Which is the weakest acid?
   b. What is the conjugate base of the acid HF?
   c. Which acid has the weakest conjugate base?
   d. Which acid has the strongest conjugate base?
5. For each of the following reactions, predict whether the equilibrium lies predominantly to the left or to the right. Explain your prediction briefly. *Use a table of acids and bases to answer this question.*
   a. $H_2S(aq) + CO_3^{2-}(aq) \rightleftharpoons HS^{-1}(aq) + HCO_3^{-1}(aq)$
   b. $HCN(aq) + SO_4^{2-}(aq) \rightleftharpoons CN^{-1}(aq) + HSO_4^{-1}(aq)$
   c. $SO_4^{2-}(aq) + CH_3CO_2H(aq) \rightleftharpoons HSO_4^{-1}(aq) + CH_3CO_2^{-1}(aq)$
6. A saturated solution of milk of magnesia, $Mg(OH)_2$, has a pH of 10.52. What is the hydronium ion concentration of the solution? What is the hydroxide ion concentration? Is the solution acidic or basic?

Problem Set #2 continues on the next page

Problem Set #2, Continued from previous page

7. The pH of a solution of $Ba(OH)_2$ is 10.66 at 25 °C. What is the hydroxide ion concentration in the solution? If the solution volume is 125 mL, how many grams of $Ba(OH)_2$ must have been dissolved?
8. An organic acid has $pK_a = 8.95$. What is its K_a value?
9. A weak base has $K_b = 1.5 \times 10^{-9}$. What is the value of K_a for the conjugate acid?
10. The ionization constant of a very weak acid, HA, is 4.0×10^{-9}. Calculate the equilibrium concentrations of H_3O^+, A^{-1} and HA in a 0.040 M solution of the acid.
11. The weak base methylamine, CH_3NH_2, has $K_b = 4.2 \times 10^{-4}$. Calculate the equilibrium hydroxide ion concentration in a 0.25 M solution of the base. What are the pH and pOH of the solution?
12. Calculate the hydronium ion concentration and pH for a 0.015 M solution of sodium formate, $NaHCO_2$. *Use a table of acids and bases to answer this question.*
13. Decide whether each of the following substances should be classified as a Lewis acid or a Lewis base.
    a. BCl_3 (Hint: draw the electron dot structure)
    b. H_2NNH_2, hydrazine (Hint: draw the electron dot structure)
    c. The reactants in the reaction:

$$Fe(s) + 5\,CO(g) \rightleftharpoons Fe(CO)_5(g)$$

Table of Acids and Bases for CH 223

Increasing Acid Strength

Increasing Base Strength

Acid Name	Acid	K_a	Base	K_b	Base Name
Perchloric acid	$HClO_4$	large	ClO_4^-	very small	perchlorate ion
Sulfuric acid	H_2SO_4	large	HSO_4^-	very small	hydrogen sulfate ion
Hydrochloric acid	HCl	large	Cl^-	very small	chloride ion
Nitric acid	HNO_3	large	NO_3^-	very small	nitrate ion
Hydronium ion	H_3O^+	1.0	H_2O	1.0×10^{-14}	water
Sulfurous acid	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	sulfate ion
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	dihydrogen phosphate ion
Hexaaquairon(III) ion	$[Fe(H_2O)_6]^{3+}$	6.3×10^{-3}	$[Fe(H_2O)_5OH]^{2+}$	1.6×10^{-12}	pentaaquahydroxoiron(III) ion
Hydrofluoric acid	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	fluoride ion
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	nitrite ion
Formic acid	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	formate ion
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	benzoate ion
Acetic acid	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	acetate ion
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	propanoate ion
Hexaaquaaluminum ion	$[Al(H_2O)_6]^{3+}$	7.9×10^{-6}	$[Al(H_2O)_5OH]^{2+}$	1.3×10^{-9}	pentaaquahydroxoaluminum ion
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	hydrogen carbonate ion
Hexaaquacopper(II) ion	$[Cu(H_2O)_6]^{2+}$	1.6×10^{-7}	$[Cu(H_2O)_5OH]^+$	6.3×10^{-8}	pentaaquahydroxocopper(II) ion
Hydrogen sulfide	H_2S	1×10^{-7}	HS^-	1×10^{-7}	hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}	hydrogen phosphate ion
Hydrogen sulfite ion	HSO_3^-	6.2×10^{-8}	SO_3^{2-}	1.6×10^{-7}	sulfite ion
Hypochlorous acid	$HClO$	3.5×10^{-8}	ClO^-	2.9×10^{-7}	hypochlorite ion
Hexaaqualead(II) ion	$[Pb(H_2O)_6]^{2+}$	1.5×10^{-8}	$[Pb(H_2O)_5OH]^+$	6.7×10^{-7}	pentaaquahydroxolead(II) ion
Hexaaquacobalt(II) ion	$[Co(H_2O)_6]^{2+}$	1.3×10^{-9}	$[Co(H_2O)_5OH]^+$	7.7×10^{-6}	pentaaquahydroxocobalt(II) ion
Boric acid	$B(OH)_3(H_2O)$	7.3×10^{-10}	$B(OH)_4^-$	1.4×10^{-5}	tetrahydroxoborate ion
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}	ammonia
Hydrocyanic acid	HCN	4.0×10^{-10}	CN^-	2.5×10^{-5}	cyanide ion
Hexaaquairon(II) ion	$[Fe(H_2O)_6]^{2+}$	3.2×10^{-10}	$[Fe(H_2O)_5OH]^+$	3.1×10^{-5}	pentaaquahydroxoiron(II) ion
Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}	carbonate ion
Hexaaquanickel(II) ion	$[Ni(H_2O)_6]^{2+}$	2.5×10^{-11}	$[Ni(H_2O)_5OH]^+$	4.0×10^{-4}	pentaaquahydroxonickel(II) ion
Hydrogen phosphate ion	HPO_4^{2-}	3.6×10^{-13}	PO_4^{3-}	2.8×10^{-2}	phosphate ion
Water	H_2O	1.0×10^{-14}	OH^-	1.0	hydroxide ion
Hydrogen sulfide ion*	HS^-	1×10^{-19}	S^{2-}	1×10^{5}	sulfide ion
Ethanol	C_2H_5OH	very small	$C_2H_5O^-$	large	ethoxide ion
Ammonia	NH_3	very small	NH_2^-	large	amide ion
Hydrogen	H_2	very small	H^-	large	hydride ion

* The values of K_a for HS^- and K_b for S^{2-} are estimates.

CH 223 Spring 2025:

Problem Set #3

Instructions

Step One (all sections):

- **Learn the material** for Problem Set #3 by **reading Chapter 14** of the textbook and/or by watching the videos found on our website (https://mhchem.org/223)
- **Try the problems** for Problem Set #3 found on the next pages on your own first. **Write out the answers (and show your work) by hand (on a tablet or paper)**; do not type your answers (and work) to avoid a point penalty. If you write the answers on the problem set itself, you will receive fewer points. Include your name on your problem set!

Step Two:

Section 01 and H1: We will go over Problem Set #3 during recitation. ***Self correct all problems*** of your problem set before turning it in at the end of recitation.

- *Section 01:* due **Monday, April 21 at 1:10 PM**
- *Section H1:* due **Wednesday, April 23 at 1:10 PM**

Section W1: **Watch the recitation video** for Problem Set #3:

http://mhchem.org/v/p.htm

- **Self correct *all* of the problems** while viewing the video. Mark correct problems with a star (or other similar mark), and correct all incorrect problems (show the correct answer and the steps required to achieve it.)
- **Submit Problem Set #3 via email (mike.russell@mhcc.edu) as a single PDF file** (use CamScanner (https://camscanner.com), CombinePDF (https://combinepdf.com), etc.) **by 11:59 PM Wednesday, April 23.**

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

CH 223 Problem Set #3

** Complete problem set on separate pieces of paper showing all work, circling final answers, etc.*
** Self correct your work before turning it in to the instructor.*

Covering: **Chapter Fourteen Part II** *and* **Chapter Guide Three**
Important Tables and/or Constants: "**Titration Guide**" *(Handout),* "**Buffers and Henderson-Hasselbalch Guide**" *(Handout)* and the **Table of Acids and Bases for CH 223** *(after this problem set),* $\mathbf{K_w = 1.00 \times 10^{-14}}$ at 25 °C

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1. Calculate the hydronium ion concentration and the pH when 50.0 mL of 0.40 M NH_3 is mixed with 50.0 mL of 0.40 M HCl. *Use a table to look up relevant K values. Hint: Determine the region this problem would use from the WB + SA Titration Calculations lab.*
2. What is the pH of the solution that results from adding 25.0 mL of 0.12 M HCl to 25.0 mL of 0.43 M NH_3? *Use a table to look up relevant K values.*
3. For each of the following, decide whether the pH is less than, equal to, or greater than 7.
    a. 150 mL of 0.20 M HNO_3 is mixed with 75 mL of 0.40 M LiOH
    b. equal volumes of 0.10 M acetic acid, CH_3CO_2H, and 0.10 M KOH are mixed
    c. 25 mL of 0.015 M NH_3 is mixed with 12 mL of 0.015 M HCl
    d. 25 mL of 0.45 M H_2SO_4 is mixed with 25 mL of 0.90 M NaOH
4. Does the pH of the solution increase, decrease or stay the same when you:
    a. Add solid sodium oxalate, $Na_2C_2O_4$, to 50.0 mL of 0.015 M oxalic acid, $H_2C_2O_4$?
    b. Add solid ammonium chloride to 75 mL of 0.016 M HCl?
    c. Add 20.0 g of NaCl to 1.0 L of 0.10 M sodium acetate, $NaCH_3CO_2$?
    d. Add 10.3 g of $FeCl_3$ to 1.0 L of pure water?
5. Which of the following combinations would be the best choice to buffer the pH of a solution at approximately 7? *Use a table to look up relevant K values.*
    a. H_3PO_4 and NaH_2PO_4
    b. NaH_2PO_4 and Na_2HPO_4
    c. Na_2HPO_4 and Na_3PO_4
6. What is the pH of 100. mL of 0.15 M acetic acid to which 1.56 g of sodium acetate, $NaCH_3CO_2$, has been added? *Use a table to look up relevant K values.*
7. Lactic acid, $CH_3CHOHCO_2H$, is found in sour milk, in sauerkraut, and in muscles after activity. K_a for lactic acid = 1.4×10^{-4}.
    a. If 2.75 g of $NaCH_3CHOHCO_2$, sodium lactate, is added to 5.00×10^2 mL of 0.100 M lactic acid, what is the pH of the resulting buffer solution?
    b. Will the pH be lower or higher than the pH of the pure lactic acid solution?
8. Calculate the pH of a solution that has an ammonium chloride concentration of 0.050 M and an ammonia concentration of 0.045 M. *Use a table to look up relevant K values.*
9. What mass of ammonium chloride, NH_4Cl, must be added to exactly 5.00×10^2 mL of 0.10 M NH_3 to give a solution with a pH of 9.00? *Use a table to look up relevant K values.*
10. A buffer solution is composed of 1.360 g of KH_2PO_4 and 5.677 g of Na_2HPO_4. *Use a table to look up relevant K values.*
    a. What is the pH of the buffer solution?
    b. What mass of KH_2PO_4 must be added to decrease the buffer solution pH by 0.5 units?

Problem Set #3 continues on the next page

11. You dissolve 0.425 g of NaOH in 2.00 L of a buffer solution that has $[H_2PO_4^-] = [HPO_4^{2-}] = 0.132$ M. What is the pH of the solution before adding the NaOH? After adding the NaOH? *Use a table to look up relevant K values.*
12. What will be the pH change when 20.0 mL of 0.100 M NaOH is added to 80.0 mL of a buffer solution consisting of 0.169 M NH_3 and 0.183 M NH_4Cl? *Use a table to look up relevant K values.*
13. Assume you dissolve 0.235 g of the weak acid benzoic acid, $C_6H_5CO_2H$, in enough water to make 1.00×10^2 mL of solution and then titrate the solution with 0.108 M NaOH. *Use a table to look up relevant K values.*

$$C_6H_5CO_2H(aq) + OH^{-1}(aq) \rightleftharpoons C_6H_5CO_2^{-1}(aq) + H_2O(\ell)$$

    a. What is the pH of the original benzoic acid solution?
    b. What are the concentrations of the following ions at the equivalence point? Na^+, H_3O^+, OH^-, and $C_6H_5CO_2^-$? What is the pH at the equivalence point?

14. A solution of the weak base aniline, $C_6H_5NH_2$, $K_b = 4.0 \times 10^{-10}$, in 25.0 mL of water requires 25.67 mL of 0.175 M HCl to reach the equivalence point.

$$C_6H_5NH_2(aq) + H_3O^+(aq) \rightleftharpoons C_6H_5NH_3^+(aq) + H_2O(\ell)$$

    a. What was the concentration of the aniline in the original solution?
    b. What are the concentrations of H_3O^+, OH^- and $C_6H_5NH_3^+$ at the equivalence point? What is the pH of the solution at the equivalence point?

Table of Acids and Bases for CH 223

Increasing Acid Strength

Increasing Base Strength

Acid Name	**Acid**	**K_a**	**Base**	**K_b**	**Base Name**
Perchloric acid	$HClO_4$	large	ClO_4^-	very small	perchlorate ion
Sulfuric acid	H_2SO_4	large	HSO_4^-	very small	hydrogen sulfate ion
Hydrochloric acid	HCl	large	Cl^-	very small	chloride ion
Nitric acid	HNO_3	large	NO_3^-	very small	nitrate ion
Hydronium ion	H_3O^+	1.0	H_2O	1.0×10^{-14}	water
Sulfurous acid	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	sulfate ion
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	dihydrogen phosphate ion
Hexaaquairon(III) ion	$[Fe(H_2O)_6]^{3+}$	6.3×10^{-3}	$[Fe(H_2O)_5OH]^{2+}$	1.6×10^{-12}	pentaaquahydroxoiron(III) ion
Hydrofluoric acid	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	fluoride ion
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	nitrite ion
Formic acid	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	formate ion
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	benzoate ion
Acetic acid	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	acetate ion
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	propanoate ion
Hexaaquaaluminum ion	$[Al(H_2O)_6]^{3+}$	7.9×10^{-6}	$[Al(H_2O)_5OH]^{2+}$	1.3×10^{-9}	pentaaquahydroxoaluminum ion
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	hydrogen carbonate ion
Hexaaquacopper(II) ion	$[Cu(H_2O)_6]^{2+}$	1.6×10^{-7}	$[Cu(H_2O)_5OH]^+$	6.3×10^{-8}	pentaaquahydroxocopper(II) ion
Hydrogen sulfide	H_2S	1×10^{-7}	HS^-	1×10^{-7}	hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}	hydrogen phosphate ion
Hydrogen sulfite ion	HSO_3^-	6.2×10^{-8}	SO_3^{2-}	1.6×10^{-7}	sulfite ion
Hypochlorous acid	$HClO$	3.5×10^{-8}	ClO^-	2.9×10^{-7}	hypochlorite ion
Hexaaqualead(II) ion	$[Pb(H_2O)_6]^{2+}$	1.5×10^{-8}	$[Pb(H_2O)_5OH]^+$	6.7×10^{-7}	pentaaquahydroxolead(II) ion
Hexaaquacobalt(II) ion	$[Co(H_2O)_6]^{2+}$	1.3×10^{-9}	$[Co(H_2O)_5OH]^+$	7.7×10^{-6}	pentaaquahydroxocobalt(II) ion
Boric acid	$B(OH)_3(H_2O)$	7.3×10^{-10}	$B(OH)_4^-$	1.4×10^{-5}	tetrahydroxoborate ion
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}	ammonia
Hydrocyanic acid	HCN	4.0×10^{-10}	CN^-	2.5×10^{-5}	cyanide ion
Hexaaquairon(II) ion	$[Fe(H_2O)_6]^{2+}$	3.2×10^{-10}	$[Fe(H_2O)_5OH]^+$	3.1×10^{-5}	pentaaquahydroxoiron(II) ion
Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}	carbonate ion
Hexaaquanickel(II) ion	$[Ni(H_2O)_6]^{2+}$	2.5×10^{-11}	$[Ni(H_2O)_5OH]^+$	4.0×10^{-4}	pentaaquahydroxonickel(II) ion
Hydrogen phosphate ion	HPO_4^{2-}	3.6×10^{-13}	PO_4^{3-}	2.8×10^{-2}	phosphate ion
Water	H_2O	1.0×10^{-14}	OH^-	1.0	hydroxide ion
Hydrogen sulfide ion*	HS^-	1×10^{-19}	S^{2-}	1×10^{5}	sulfide ion
Ethanol	C_2H_5OH	very small	$C_2H_5O^-$	large	ethoxide ion
Ammonia	NH_3	very small	NH_2^-	large	amide ion
Hydrogen	H_2	very small	H^-	large	hydride ion

* The values of K_a for HS^- and K_b for S^{2-} are estimates.

CH 223 Exam Prep I Worksheet Name: ____

Worksheet due dates: **<u>Mon, 4/28</u>, 1:10 PM** *(01)* **, <u>Wed, 4/30</u>, 1:10 PM** *(H1)* ***or*** **11:59 PM** *(W1, email)*. To complete, show ***detailed*** *steps* on how to get the given answer for each problem. *Failure to use this form for work and answers will result in a point penalty.*

<u>Problem 1</u>: Consider the following equilibrium: **$2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$** *where* **$K = 1.6 * 10^{-5}$**
1.0 mol of pure NOCl ***and*** 1.0 mol of pure Cl_2 are placed in a 1.00 L container. Calculate the equilibrium concentration of NO(g) and $Cl_2(g)$. *To receive credit, show a complete ICE table.*

Answer to Problem #1: **$[NO(g)] = 4.0 * 10^{-3}$ M, $[Cl_2(g)] = 1.0$ M**

<u>Problem 2</u>: How many moles of benzoic acid, a monoprotic acid with $K_a = 6.4 * 10^{-5}$, must be dissolved in 500. mL of H_2O to produce a solution with pH = 2.50?

Answer to Problem #2: **$7.9 * 10^{-2}$ mol** *(answers ±0.1 ok, depends on method used to solve)*

<u>Problem 3</u>: Complete the following problems using correct significant figures:

$[H^+] = 0.001501$ M, and pH = ____________

$pK_b = 10.35$, and K_b = ____________

Problem 4: You have solutions of 0.200 M HNO_2 and 0.200 M KNO_2 (K_a for $HNO_2 = 4.00 * 10^{-4}$). A buffer of pH 3.00 is needed. What volumes of HNO_2 and KNO_2 are required to make 1 liter of buffered solution? *(Hints: 1000 mL = $V_{wa} + V_{wb}$* ***and:*** *rewrite Henderson-Hasselbalch, substituting n_{wb}/n_{wa} for $C_{wb}V_{wb}/C_{wa}V_{wa}$ (because $n_{wa} = C_{wa}V_{wa}$, etc.))*

Answer to Problem #4: **715 mL of HNO_2 and 285 mL of KNO_2, ±1 mL ok**

Problem 5: What is the pH of a solution that results when 0.010 mol HNO_3 is added to 500. mL of a solution that is 0.10 M in aqueous ammonia and 0.20 M in ammonium nitrate? Assume no volume change, and K_b for $NH_3 = 1.8 * 10^{-5}$)

Answer to Problem #5: **pH = 8.82**

Problem 6: You dissolve 1.00 g of an unknown diprotic acid in 200.0 mL of H_2O. The solution is just neutralized by 5.00 mL of a 1.00 M NaOH solution. What is the molar mass of the unknown acid?

Answer to Problem #6: **400. g/mol**

CH 223 Spring 2025:

Problem Set #4

Instructions

Step One (all sections):

- **Learn the material** for Problem Set #4 by **reading Chapter 15 and Chapter 16** of the textbook and/or by watching the videos found on our website (https://mhchem.org/223)
- **Try the problems** for Problem Set #4 found on the next pages on your own first. **Write out the answers (and show your work) by hand (on a tablet or paper)**; do not type your answers (and work) to avoid a point penalty. If you write the answers on the problem set itself, you will receive fewer points. Include your name on your problem set!

Step Two:

Section 01 and H1: We will go over Problem Set #4 during recitation. ***Self correct all problems*** of your problem set before turning it in at the end of recitation.

- *Section 01:* due **Monday, May 12 at 1:10 PM**
- *Section H1:* due **Wednesday, May 14 at 1:10 PM**

Section W1: **Watch the recitation video** for Problem Set #4:

http://mhchem.org/v/r.htm

- **Self correct *all* of the problems** while viewing the video. Mark correct problems with a star (or other similar mark), and correct all incorrect problems (show the correct answer and the steps required to achieve it.)
- **Submit Problem Set #4 via email (mike.russell@mhcc.edu) as a single PDF file** (use CamScanner (https://camscanner.com), CombinePDF (https://combinepdf.com), etc.) **by 11:59 PM Wednesday, May 14.**

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

CH 223 Problem Set #4

** Complete problem set on separate pieces of paper showing all work, circling final answers, etc.*
** Self correct your work before turning it in to the instructor.*

Covering: **Chapter Fifteen** (solubility), **Chapter Sixteen** *and* **Chapter Guide Four**
Important Tables and/or Constants: **Solubility Table** (*from the CH 221* Net Ionics *lab* or here: **https://mhchem.org/sol**), **"Solubility Product Constant (K_{sp}) Values at 25 °C"** *and* "**Complex Ion Formation Constant (K_f) Values at 25 °C"** *at the end of problem set #4*, "**Solubility Guide**" *(Handout)*, **Table of Thermodynamic Values** *(found at the end of CH 223 Problem Set #5 or here:* **http://mhchem.org/thermo**)

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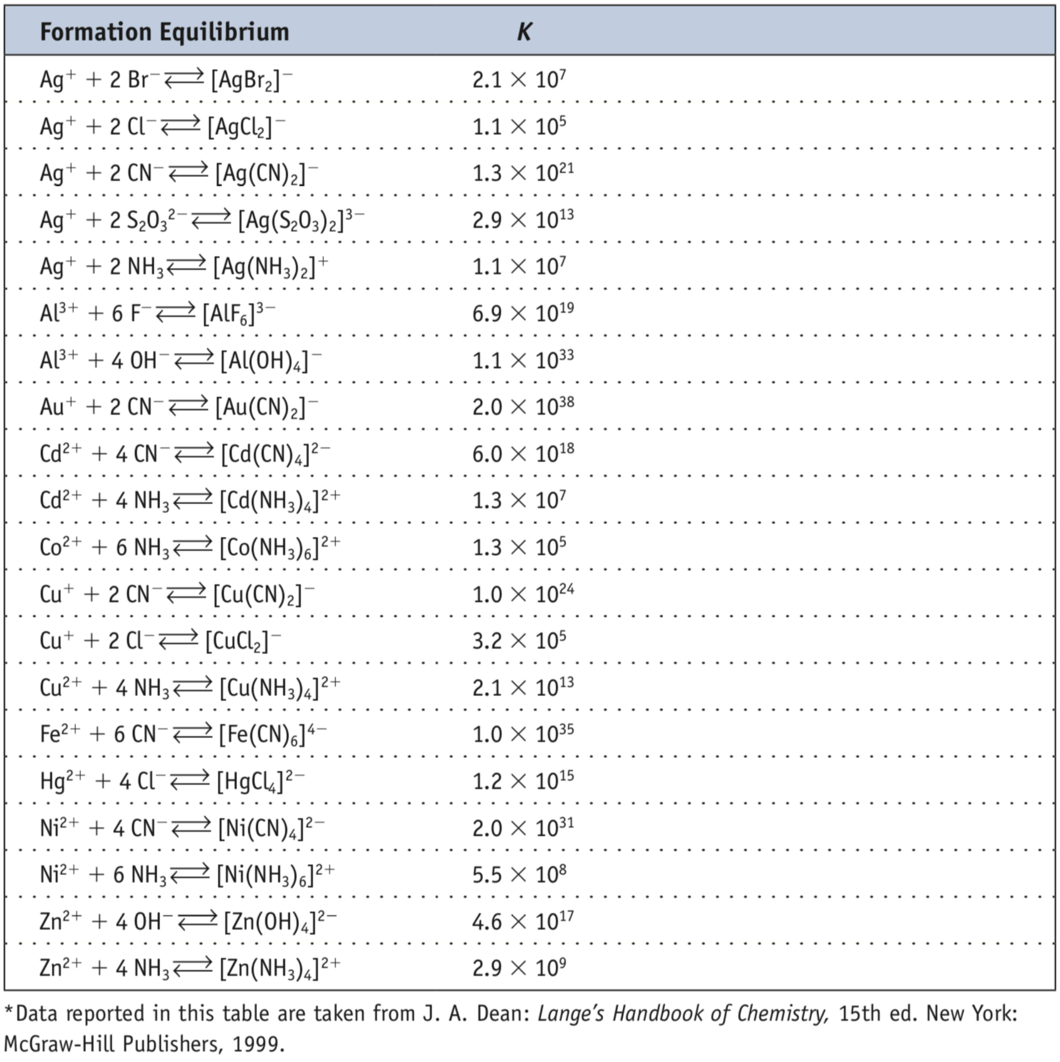
1. Using a solubility table, predict whether the following are insoluble or soluble in water.
    a. $Pb(NO_3)_2$
    b. $Fe(OH)_3$
    c. $ZnCl_2$
    d. CuS
2. a. For **$PbSO_4$** *and* **BaF_2**, (i) write a balanced equation showing the equilibrium occurring when each insoluble salt is added separately to water, and (ii) write the K_{sp} expression.
   b. Write a balanced equation showing the equilibrium occurring for the formation of the complex ion **$Zn(NH_3)_4^{2+}$**(aq) and write the corresponding K_f expression.
3. At 20 °C, a saturated aqueous solution of silver acetate, $AgCH_3CO_2$, contains 0.74 g of the silver compound dissolved in 100.0 mL of solution. Calculate K_{sp} for silver acetate.
$$AgCH_3CO_2(s) \rightleftharpoons Ag^+(aq) + CH_3CO_2^{-1}(aq)$$
4. What is the molar concentration of Au^+(aq) in a saturated solution of AuCl ($K_{sp} = 2.0 \times 10^{-13}$) in pure water at 25 °C? The equation:
$$AuCl(s) \rightleftharpoons Au^+(aq) + Cl^-(aq)$$
5. Estimate the solubility of lead(II) bromide (a) in moles per liter and (b) in grams per liter of pure water. (K_{sp} for lead(II) bromide = 6.6×10^{-6})
6. If 75 mg of lead(II) sulfate is placed in 250 mL of pure water, does all of it dissolve? If not, how much dissolves? (K_{sp} for lead(II) sulfate = 2.5×10^{-8})
7. You place 2.234 g of solid $Ca(OH)_2$ in 1.00 L of pure water at 25 °C. The pH of the solution is found to be 12.68. Estimate the K_{sp} for $Ca(OH)_2$.
8. Which compound in each of the following pairs is the more soluble?
    a. AgBr ($K_{sp} = 5.0 \times 10^{-13}$) or AgSCN ($K_{sp} = 1.0 \times 10^{-12}$)
    b. $SrCO_3$ ($K_{sp} = 9.3 \times 10^{-10}$) or $SrSO_4$ ($K_{sp} = 3.4 \times 10^{-7}$)
    c. AgI ($K_{sp} = 8.3 \times 10^{-17}$) or PbI_2 ($K_{sp} = 9.8 \times 10^{-9}$)
9. What is the solubility, in milligrams per milliliter, of BaF_2 (a) in pure water, and (b) in water containing 5.0 mg/mL KF? (K_{sp} for BaF_2 = 1.8×10^{-7})
10. Sodium carbonate is added to a solution in which the concentration of Ni^{2+} ion is 0.0024 M. Will precipitation of $NiCO_3$ ($K_{sp} = 1.4 \times 10^{-7}$) occur (a) when the concentration of the carbonate ion is 1.0×10^{-6} M or (b) when it is 100 times greater (or 1.0×10^{-4} M)? The equation: $NiCO_3(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$
11. You have 95 mL of a solution that has a lead(II) concentration of 0.0012 M. Will $PbCl_2$ precipitate when 1.20 g of solid NaCl is added? (K_{sp} for $PbCl_2$ = 1.7×10^{-5})

Problem Set #4 continues on the next page

12. Solid silver(I) iodide, AgI, can be dissolved by adding aqueous sodium cyanide to it (see equation below.) Show that this equation is the sum of two other equations, one for dissolving AgI ($K_{sp} = 8.3 \times 10^{-17}$) to give its ions and the other for the formation of the $[Ag(CN)_2]^{-1}$ ion ($K_f = 1.3 \times 10^{21}$) from Ag^+ and CN^{-1}. Calculate K_{net} for the overall reaction. The equation: $AgI(s) + 2\,CN^{-1}(aq) \rightleftharpoons [Ag(CN)_2]^{-1}(aq) + I^-(aq)$

13. You have a solution with aqueous Cu^{2+} and Ag^+ ions. Using a table of solubility product constants, devise a way to separate these ions by adding one reagent to precipitate one of them as an insoluble salt and leave the other in solution.
14. A solution contains 0.10 M iodide ion, I^{-1}, and 0.10 M carbonate ion, CO_3^{2-}.
    a. If solid $Pb(NO_3)_2$ is slowly added to the solution, which salt will precipitate first, PbI_2 or $PbCO_3$? (K_{sp} for $PbI_2 = 9.8 \times 10^{-9}$, K_{sp} for $PbCO_3 = 7.4 \times 10^{-14}$)
    b. What will be the concentration of the first ion that precipitates (CO_3^{2-} or I^{-1}) when the second, more soluble salt begins to precipitate?
15. Which substance has the higher entropy in each of the following pairs?
    a. a sample of pure silicon (to be used in a computer chip) or a piece of silicon containing traces of other elements such as boron or phosphorus
    b. $O_2(g)$ at 0 °C or $O_2(g)$ at -50 °C
    c. $I_2(s)$ or $I_2(g)$, both at room temperature
    d. $C_2H_4(g)$ or $N_2(g)$ (two substances with the same molar mass)
16. Using a table of $S°$ values, calculate the entropy change, $\Delta S°$, for each of the following changes and comment on the sign of the change.
    a. $C_2H_5OH(\ell) \rightarrow C_2H_5OH(g)$
    b. $CCl_4(g) \rightarrow CCl_4(\ell)$
17. Calculate the standard molar entropy change of formation ($\Delta S_f°$) for each of the following compounds from the elements at 25 °C.
    a. $H_2S(g)$ (*Note:* sulfur is an octamer (S_8))
    b. $Li_2CO_3(s)$

Complex Ion Formation Constant (K_f) Values at 25 °C



Formation Equilibrium	*K*
$Ag^+ + 2\ Br^- \rightleftarrows [AgBr_2]^-$	2.1×10^7
$Ag^+ + 2\ Cl^- \rightleftarrows [AgCl_2]^-$	1.1×10^5
$Ag^+ + 2\ CN^- \rightleftarrows [Ag(CN)_2]^-$	1.3×10^{21}
$Ag^+ + 2\ S_2O_3{}^{2-} \rightleftarrows [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
$Ag^+ + 2\ NH_3 \rightleftarrows [Ag(NH_3)_2]^+$	1.1×10^7
$Al^{3+} + 6\ F^- \rightleftarrows [AlF_6]^{3-}$	6.9×10^{19}
$Al^{3+} + 4\ OH^- \rightleftarrows [Al(OH)_4]^-$	1.1×10^{33}
$Au^+ + 2\ CN^- \rightleftarrows [Au(CN)_2]^-$	2.0×10^{38}
$Cd^{2+} + 4\ CN^- \rightleftarrows [Cd(CN)_4]^{2-}$	6.0×10^{18}
$Cd^{2+} + 4\ NH_3 \rightleftarrows [Cd(NH_3)_4]^{2+}$	1.3×10^7
$Co^{2+} + 6\ NH_3 \rightleftarrows [Co(NH_3)_6]^{2+}$	1.3×10^5
$Cu^+ + 2\ CN^- \rightleftarrows [Cu(CN)_2]^-$	1.0×10^{24}
$Cu^+ + 2\ Cl^- \rightleftarrows [CuCl_2]^-$	3.2×10^5
$Cu^{2+} + 4\ NH_3 \rightleftarrows [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
$Fe^{2+} + 6\ CN^- \rightleftarrows [Fe(CN)_6]^{4-}$	1.0×10^{35}
$Hg^{2+} + 4\ Cl^- \rightleftarrows [HgCl_4]^{2-}$	1.2×10^{15}
$Ni^{2+} + 4\ CN^- \rightleftarrows [Ni(CN)_4]^{2-}$	2.0×10^{31}
$Ni^{2+} + 6\ NH_3 \rightleftarrows [Ni(NH_3)_6]^{2+}$	5.5×10^8
$Zn^{2+} + 4\ OH^- \rightleftarrows [Zn(OH)_4]^{2-}$	4.6×10^{17}
$Zn^{2+} + 4\ NH_3 \rightleftarrows [Zn(NH_3)_4]^{2+}$	2.9×10^9

*Data reported in this table are taken from J. A. Dean: *Lange's Handbook of Chemistry,* 15th ed. New York: McGraw-Hill Publishers, 1999.

Solubility Product Constant (K_{sp}) Values at 25 °C

Cation	Compound	K_{sp}
Ba^{2+}	*$BaCrO_4$	1.2×10^{-10}
	$BaCO_3$	2.6×10^{-9}
	BaF_2	1.8×10^{-7}
	*$BaSO_4$	1.1×10^{-10}
Ca^{2+}	$CaCO_3$ (calcite)	3.4×10^{-9}
	*CaF_2	5.3×10^{-11}
	*$Ca(OH)_2$	5.5×10^{-5}
	$CaSO_4$	4.9×10^{-5}
Cu^+, Cu^{2+}	$CuBr$	6.3×10^{-9}
	CuI	1.3×10^{-12}
	$Cu(OH)_2$	2.2×10^{-20}
	$CuSCN$	1.8×10^{-13}
Au^+	$AuCl$	2.0×10^{-13}
Fe^{2+}	$FeCO_3$	3.1×10^{-11}
	$Fe(OH)_2$	4.9×10^{-17}
Pb^{2+}	$PbBr_2$	6.6×10^{-6}
	$PbCO_3$	7.4×10^{-14}
	$PbCl_2$	1.7×10^{-5}
	$PbCrO_4$	2.8×10^{-13}
	PbF_2	3.3×10^{-8}
	PbI_2	9.8×10^{-9}
	$Pb(OH)_2$	1.4×10^{-15}
	$PbSO_4$	2.5×10^{-8}
Mg^{2+}	$MgCO_3$	6.8×10^{-6}
	MgF_2	5.2×10^{-11}
	$Mg(OH)_2$	5.6×10^{-12}
Mn^{2+}	$MnCO_3$	2.3×10^{-11}
	*$Mn(OH)_2$	1.9×10^{-13}
$Hg_2{}^{2+}$	*Hg_2Br_2	6.4×10^{-23}
	Hg_2Cl_2	1.4×10^{-18}
	*Hg_2I_2	2.9×10^{-29}
	Hg_2SO_4	6.5×10^{-7}
Ni^{2+}	$NiCO_3$	1.4×10^{-7}
	$Ni(OH)_2$	5.5×10^{-16}
Ag^+	*$AgBr$	5.4×10^{-13}
	*$AgBrO_3$	5.4×10^{-5}
	$AgCH_3CO_2$	1.9×10^{-3}
	$AgCN$	6.0×10^{-17}
	Ag_2CO_3	8.5×10^{-12}
	*$Ag_2C_2O_4$	5.4×10^{-12}
	*$AgCl$	1.8×10^{-10}
	Ag_2CrO_4	1.1×10^{-12}
	*AgI	8.5×10^{-17}
	$AgSCN$	1.0×10^{-12}
	*Ag_2SO_4	1.2×10^{-5}
Sr^{2+}	$SrCO_3$	5.6×10^{-10}
	SrF_2	4.3×10^{-9}
	$SrSO_4$	3.4×10^{-7}
Tl^+	$TlBr$	3.7×10^{-6}
	$TlCl$	1.9×10^{-4}
	TlI	5.5×10^{-8}
Zn^{2+}	$Zn(OH)_2$	3×10^{-17}
	$Zn(CN)_2$	8.0×10^{-12}

The values reported in this table were taken from J. A. Dean: *Lange's Handbook of Chemistry,* 15th ed. New York: McGraw-Hill Publishers, 1999. Values have been rounded off to two significant figures.

*Calculated solubility from these K_{sp} values will match experimental solubility for this compound within a factor of 2. Experimental values for solubilities are given in R. W. Clark and J. M. Bonicamp: *Journal of Chemical Education,* Vol. 75, p. 1182, 1998.

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CH 223 Spring 2025:

Problem Set #5

Instructions

Step One (all sections):

- **Learn the material** for Problem Set #5 by **reading Chapter 16 and Chapter 17** of the textbook and/or by watching the videos found on our website (https://mhchem.org/223)
- **Try the problems** for Problem Set #5 found on the next pages on your own first. **Write out the answers (and show your work) by hand (on a tablet or paper)**; do not type your answers (and work) to avoid a point penalty. If you write the answers on the problem set itself, you will receive fewer points. Include your name on your problem set!

Step Two:

Section 01 and H1: We will go over Problem Set #5 during recitation. ***Self correct all problems*** of your problem set before turning it in at the end of recitation.

- *Section 01:* due **Monday, May 19 at 1:10 PM**
- *Section H1:* due **Wednesday, May 21 at 1:10 PM**

Section W1: **Watch the recitation video** for Problem Set #5:

http://mhchem.org/v/t.htm

- **Self correct *all* of the problems** while viewing the video. Mark correct problems with a star (or other similar mark), and correct all incorrect problems (show the correct answer and the steps required to achieve it.)
- **Submit Problem Set #5 via email (mike.russell@mhcc.edu) as a single PDF file** (use CamScanner (https://camscanner.com), CombinePDF (https://combinepdf.com), etc.) **by 11:59 PM Wednesday, May 21.**

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

CH 223 Problem Set #5

** Complete problem set on separate pieces of paper showing all work, circling final answers, etc.*
** Self correct your work before turning it in to the instructor.*

Covering: **Chapter Sixteen, Chapter Seventeen** *and* **Chapter Guide Five**
Important Tables and/or Constants: **F = 96485 C/mol e$^-$, R = 8.3145 J mol^{-1} K^{-1}**, "**Redox Reactions**" *(Handout),* **Table of Redox Potentials** *at the end of this problem set,* **Table of Thermodynamic values** *at the end of this problem set and here:* **http://mhchem.org/thermo**

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1. Classify each of the reactions according to their spontaneity. Are these reactions enthalpy and/or entropy driven?
   a. $C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(\ell)$ $\Delta H° = -673$ kJ $\Delta S° = 60.4$ J/K
   b. $MgO(s) + C(graphite) \rightarrow Mg(s) + CO(g)$ $\Delta H° = 490.7$ kJ $\Delta S° = 197.9$ J/K
2. Use a Table to calculate $\Delta H°$ and $\Delta S°$ for the reaction of silicon(IV) oxide with carbon:
   $$SiO_2(s) + C(graphite) \rightarrow Si(s) + CO_2(g)$$
   a. Is the reaction spontaneous at 298 K?
   b. Is the reaction predicted to be spontaneous at higher temperatures?
3. Using values of $\Delta H°_f$ and $S°$, calculate $\Delta G°_{rxn}$ for each of the following reactions. Which of these reactions is (are) predicted to be product-favored? Are the reactions enthalpy or entropy driven?
   a. $Ba(s) + 2\,H_2O(\ell) \rightarrow Ba(OH)_2(aq) + 2\,H_2(g)$
      (*Note:* for $Ba(OH)_2(aq)$, $\Delta H° = -1002.82$ kJ/mol and $S° = 74.5$ J K^{-1} mol^{-1})
   b. $6\,C(graphite) + 3\,H_2(g) \rightarrow C_6H_6(\ell)$
4. Using values of $\Delta G°_f$, calculate $\Delta G°_{rxn}$ for each of the following reactions. Which are product-favored?
   a. $HgS(s, red) + O_2(g) \rightarrow Hg(\ell) + SO_2(g)$
   b. $2\,H_2S(g) + 3\,O_2(g) \rightarrow 2\,H_2O(g) + 2\,SO_2(g)$
5. Estimate the temperature required to decompose $CaSO_4(s)$ into $CaO(s)$ and $SO_3(g)$ using values of $\Delta H°_f$ and $S°$.
6. The formation of $O_3(g)$ from $O_2(g)$ has a standard free energy change, $\Delta G°$, of +163.2 kJ/mol at 25 °C. Calculate K_p at this temperature. Comment on the connection between the sign of $\Delta G°$ and the magnitude of K_p.
7. Write balanced equations for the following half-reactions. Specify whether each is an oxidation or reduction.
   a. $H_2C_2O_4(aq) \rightarrow CO_2(g)$ (in acid)
   b. $NO_3^{-1}(aq) \rightarrow NO(g)$ (in acid)
   c. $MnO_4^{-1}(aq) \rightarrow MnO_2(s)$ (in base)
8. Balance the following redox equations. All occur in acid solution.
   a. $Sn(s) + H^+(aq) \rightarrow Sn^{2+}(aq) + H_2(g)$
   b. $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$

Problem Set #5 continues on the next page

Problem Set #5, Continued from previous page

9. Balance the following redox reactions. All occur in basic solution.
    a. $NiO_2(s) + Zn(s) \rightarrow Ni(OH)_2(s) + Zn(OH)_2(s)$
    b. $Fe(OH)_2(s) + CrO_4^{2-}(aq) \rightarrow Fe(OH)_3(s) + [Cr(OH)_4]^{-1}$
10. The following **voltaic** cell is created: $Ag(s) \mid Ag^+(aq) \parallel Cl_2(g, 1\ atm) \mid Cl^{-1}(aq, 1.0\ M) \mid Pt(s)$
    a. Write equations for the oxidation and reduction half-reactions and for the overall (cell) reaction.
    b. Which half-reaction occurs in the anode compartment and which occurs in the cathode compartment?
    c. Complete the following sentences: Electrons in the external circuit flow from the _____ electrode to the _____ electrode. Negative ions move in the salt bridge from the _____ half-cell to the _____ half-cell.
11. Balance each of the following unbalanced equations, then calculate the standard reduction potential, $E°$, and decide whether each is product-favored as written. All reactions occur in acidic solution.
    a. $Fe^{2+}(aq) + Cu^{2+}(aq) \rightarrow Cu(s) + Fe^{3+}(aq)$
    b. $MnO_4^{-1}(aq) + NO(g) \rightarrow Mn^{2+}(aq) + NO_3^{-1}(aq)$
12. Calculate the potential at 298 K developed by a voltaic cell using the following reaction if all dissolved species are 0.015 M: (hint: use the Nernst equation!)

$$2\ Fe^{2+}(aq) + H_2O_2(aq) + 2\ H^+(aq) \rightarrow 2\ Fe^{3+}(aq) + 2\ H_2O(\ell)$$

13. Calculate $\Delta G°$ and the equilibrium constant for the following reaction:

$$Cu(s) + 2\ Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$$

14. In the electrolysis of a solution containing $Ag^+(aq)$, metallic $Ag(s)$ deposits on the cathode. Using a current of 1.12 A for 2.40 h, what mass of silver forms?

Standard Reduction Potentials in Aqueous Solution at 25 °C

Reduction Half-Reaction		**E° (V)**
$F_2(g) + 2\ e^-$	$\longrightarrow 2\ F^-(aq)$	+2.87
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^-$	$\longrightarrow 2\ H_2O(\ell)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$	$\longrightarrow PbSO_4(s) + 2\ H_2O(\ell)$	+1.685
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$	$\longrightarrow Mn^{2+}(aq) + 4\ H_2O(\ell)$	+1.51
$Au^{3+}(aq) + 3\ e^-$	$\longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2\ e^-$	$\longrightarrow 2\ Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^-$	$\longrightarrow 2\ Cr^{3+}(aq) + 7\ H_2O\ (\ell)$	+1.33
$O_2(g) + 4\ H^+(aq) + 4\ e^-$	$\longrightarrow 2\ H_2O(\ell)$	+1.229
$Br_2(\ell) + 2\ e^-$	$\longrightarrow 2\ Br^-(aq)$	+1.08
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^-$	$\longrightarrow NO(g) + 2\ H_2O(\ell)$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2\ e^-$	$\longrightarrow Cl^-(aq) + 2\ OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2\ e^-$	$\longrightarrow Hg(\ell)$	+0.855
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	+0.799
$Hg_2^{2+}(aq) + 2\ e^-$	$\longrightarrow 2\ Hg(\ell)$	+0.789
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	+0.771
$I_2(s) + 2\ e^-$	$\longrightarrow 2\ I^-(aq)$	+0.535
$O_2(g) + 2\ H_2O(\ell) + 4\ e^-$	$\longrightarrow 4\ OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2\ e^-$	$\longrightarrow Cu(s)$	+0.337
$Sn^{4+}(aq) + 2\ e^-$	$\longrightarrow Sn^{2+}(aq)$	+0.15
$2\ H^+(aq) + 2\ e^-$	$\longrightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2\ e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2\ e^-$	$\longrightarrow Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\longrightarrow V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2\ e^-$	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2\ e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\ e^-$	$\longrightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2\ e^-$	$\longrightarrow Zn(s)$	−0.763
$2\ H_2O(\ell) + 2\ e^-$	$\longrightarrow H_2(g) + 2\ OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3\ e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2\ e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.714
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.925
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.045

Increasing strength of oxidizing agents ↑

Increasing strength of reducing agents ↓

* In volts (V) versus the standard hydrogen electrode.

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/K•mol)
aluminum			
$Al(s)$	0	0	28.3
$Al(g)$	324.4	285.7	164.54
$Al_2O_3(s)$	–1676	–1582	50.92
$AlF_3(s)$	–1510.4	–1425	66.5
$AlCl_3(s)$	–704.2	–628.8	110.67
$AlCl_3\cdot 6H_2O(s)$	–2691.57	–2269.40	376.56
$Al_2S_3(s)$	–724.0	–492.4	116.9
$Al_2(SO_4)_3(s)$	–3445.06	–3506.61	239.32
antimony			
$Sb(s)$	0	0	45.69
$Sb(g)$	262.34	222.17	180.16
$Sb_4O_6(s)$	–1440.55	–1268.17	220.92
$SbCl_3(g)$	–313.8	–301.2	337.80
$SbCl_5(g)$	–394.34	–334.29	401.94
$Sb_2S_3\mathrm{(s)}$	–174.89	–173.64	182.00
$SbCl_3\mathrm{(s)}$	–382.17	–323.72	184.10
$SbOCl\mathrm{(s)}$	–374.0	-	-
arsenic			
$As(s)$	0	0	35.1
$As(g)$	302.5	261.0	174.21
$As_4(g)$	143.9	92.4	314
$As_4O_6(s)$	–1313.94	–1152.52	214.22
$As_2O_5(s)$	–924.87	–782.41	105.44
$AsCl_3(g)$	–261.50	–248.95	327.06
$As_2S_3(s)$	–169.03	–168.62	163.59
$AsH_3(g)$	66.44	68.93	222.78
$H_3AsO_4(s)$	–906.3	—	—
barium			
$Ba(s)$	0	0	62.5
$Ba(g)$	180	146	170.24
$BaO(s)$	–548.0	–520.3	72.1
$BaCl_2(s)$	–855.0	–806.7	123.7
$BaSO_4(s)$	–1473.2	–1362.3	132.2
beryllium			
$Be(s)$	0	0	9.50
$Be(g)$	324.3	286.6	136.27
$BeO(s)$	–609.4	–580.1	13.8
bismuth			
$Bi(s)$	0	0	56.74
$Bi(g)$	207.1	168.2	187.00
$Bi_2O_3(s)$	–573.88	–493.7	151.5
$BiCl_3(s)$	–379.07	–315.06	176.98
$Bi_2S_3(s)$	–143.1	–140.6	200.4
boron			
$B(s)$	0	0	5.86
$B(g)$	565.0	521.0	153.4
$B_2O_3(s)$	–1273.5	–1194.3	53.97
$B_2H_6(g)$	36.4	87.6	232.1
$H_3BO_3(s)$	–1094.33	–968.92	88.83
$BF_3(g)$	–1136.0	–1119.4	254.4
$BCl_3(g)$	–403.8	–388.7	290.1
$B_3N_3H_6(l)$	–540.99	–392.79	199.58

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/K•mol)
boron *continued*			
$HBO_2(s)$	–794.25	–723.41	37.66
bromine			
$Br_2(l)$	0	0	152.23
$Br_2(g)$	30.91	3.142	245.5
$Br(g)$	111.88	82.429	175.0
$BrF_3(g)$	–255.60	–229.45	292.42
$HBr(g)$	–36.3	–53.43	198.7
cadmium			
$Cd(s)$	0	0	51.76
$Cd(g)$	112.01	77.41	167.75
$CdO(s)$	–258.2	–228.4	54.8
$CdCl_2(s)$	–391.5	–343.9	115.3
$CdSO_4(s)$	–933.3	–822.7	123.0
$CdS(s)$	–161.9	–156.5	64.9
calcium			
$Ca(s)$	0	0	41.6
$Ca(g)$	178.2	144.3	154.88
$CaO(s)$	–634.9	–603.3	38.1
$Ca(OH)_2(s)$	–985.2	–897.5	83.4
$CaSO_4(\mathrm{s})$	–1434.5	–1322.0	106.5
$CaSO_4 \cdot 2H_2O(s)$	–2022.63	–1797.45	194.14
$CaCO_3(s)$ (calcite)	–1220.0	–1081.4	110.0
$CaSO_3 \cdot H_2O(s)$	–1752.68	–1555.19	184.10
carbon			
$C(s)$ (graphite)	0	0	5.740
$C(s)$ (diamond)	1.89	2.90	2.38
$C(g)$	716.681	671.2	158.1
$CO(g)$	–110.52	–137.15	197.7
$CO_2(g)$	–393.51	–394.36	213.8
$CH_4(g)$	–74.6	–50.5	186.3
$CH_3OH(l)$	–239.2	–166.6	126.8
$CH_3OH(g)$	–201.0	–162.3	239.9
$CCl_4(l)$	–128.2	–62.5	214.4
$CCl_4(g)$	–95.7	–58.2	309.7
$CHCl_3(l)$	–134.1	–73.7	201.7
$CHCl_3(g)$	–103.14	–70.34	295.71
$CS_2(l)$	89.70	65.27	151.34
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	–84.0	–32.0	229.2
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50
$C_2H_5OH(l)$	–277.6	–174.8	160.7
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/K•mol)
carbon *continued*			
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
chlorine			
$Cl2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$ClF(g)$	–54.48	–55.94	217.78
$ClF_3(g)$	–158.99	–118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	–92.307	–95.299	186.9
$HClO_4(l)$	–40.58	—	—
chromium			
$Cr(s)$	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$Cr_2O_3(s)$	–1139.7	–1058.1	81.2
$CrO_3(s)$	–589.5	—	—
$(NH_4)_2Cr_2O_7(s)$	–1806.7	—	—
cobalt			
$Co(s)$	0	0	30.0
$CoO(s)$	–237.9	–214.2	52.97
$Co_3O_4(s)$	–910.02	–794.98	114.22
$Co(NO_3)_2(s)$	–420.5	—	—
copper			
$Cu(s)$	0	0	33.15
$Cu(g)$	338.32	298.58	166.38
$CuO(s)$	–157.3	–129.7	42.63
$Cu_2O(s)$	–168.6	–146.0	93.14
$CuS(s)$	–53.1	–53.6	66.5
$Cu_2S(s)$	–79.5	–86.2	120.9
$CuSO_4(s)$	–771.36	–662.2	109.2
$Cu(NO_3)_2(s)$	–302.9	—	—
fluorine			
$F_2(g)$	0	0	202.8
$F(g)$	79.4	62.3	158.8
$F_2O(g)$	24.7	41.9	247.43
$HF(g)$	–273.3	–275.4	173.8
hydrogen			
$H_2(g)$	0	0	130.7
$H(g)$	217.97	203.26	114.7
$H_2O(l)$	–285.83	–237.1	70.0
$H_2O(g)$	–241.82	–228.59	188.8
$H_2O_2(l)$	–187.78	–120.35	109.6
$H_2O_2(g)$	–136.3	–105.6	232.7
$HF(g)$	–273.3	–275.4	173.8
$HCl(g)$	–92.307	–95.299	186.9
$HBr(g)$	–36.3	–53.43	198.7
$HI(g)$	26.48	1.70	206.59

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/K•mol)
hydrogen *continued*			
$H_2S(g)$	–20.6	–33.4	205.8
$H_2Se(g)$	29.7	15.9	219.0
iodine			
$I_2(s)$	0	0	116.14
$I_2(g)$	62.438	19.3	260.7
$I(g)$	106.84	70.2	180.8
$IF(g)$	95.65	–118.49	236.06
$ICl(g)$	17.78	–5.44	247.44
$IBr(g)$	40.84	3.72	258.66
$IF_7(g)$	–943.91	–818.39	346.44
$HI(g)$	26.48	1.70	206.59
iron			
$Fe(s)$	0	0	27.3
$Fe(g)$	416.3	370.7	180.5
$Fe_2O_3(s)$	–824.2	–742.2	87.40
$Fe_3O_4(s)$	–1118.4	–1015.4	146.4
$Fe(CO)_5(l)$	–774.04	–705.42	338.07
$Fe(CO)_5(g)$	–733.87	–697.26	445.18
$FeCl_2(s)$	–341.79	–302.30	117.95
$FeCl_3(s)$	–399.49	–334.00	142.3
$FeO(s)$	–272.0	–255.2	60.75
$Fe(OH)_2(s)$	–569.0	–486.5	88.
$Fe(OH)_3(s)$	–823.0	–696.5	106.7
$FeS(s)$	–100.0	–100.4	60.29
$Fe_3C(s)$	25.10	20.08	104.60
lead			
$Pb(s)$	0	0	64.81
$Pb(g)$	195.2	162.	175.4
$PbO(s)$ (yellow)	–217.32	–187.89	68.70
$PbO(s)$ (red)	–218.99	–188.93	66.5
$Pb(OH)_2(s)$	–515.9	—	—
$PbS(s)$	–100.4	–98.7	91.2
$Pb(NO_3)_2(s)$	–451.9	—	—
$PbO_2(s)$	–277.4	–217.3	68.6
$PbCl_2(s)$	–359.4	–314.1	136.0
lithium			
$Li(s)$	0	0	29.1
$Li(g)$	159.3	126.6	138.8
$LiH(s)$	–90.5	–68.3	20.0
$LiOH(s)$	–487.5	–441.5	42.8
$LiF(s)$	–616.0	–587.5	35.7
$Li_2CO_3(s)$	–1216.04	–1132.19	90.17
manganese			
$Mn(s)$	0	0	32.0
$Mn(g)$	280.7	238.5	173.7
$MnO(s)$	–385.2	–362.9	59.71
$MnO_2(s)$	–520.03	–465.1	53.05
$Mn_2O_3(s)$	–958.97	–881.15	110.46
$Mn_3O_4(s)$	–1378.83	–1283.23	155.64
mercury			
$Hg(l)$	0	0	75.9

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/K•mol)
mercury *continued*			
$Hg(g)$	61.4	31.8	175.0
$HgO(s)$ (red)	–90.83	–58.5	70.29
$HgO(s)$ (yellow)	–90.46	–58.43	71.13
$HgCl_2(s)$	–224.3	–178.6	146.0
$Hg_2Cl_2(s)$	–265.4	–210.7	191.6
$HgS(s)$ (red)	–58.16	–50.6	82.4
$HgS(s)$ (black)	–53.56	–47.70	88.28
$HgSO_4(s)$	–707.51	–594.13	0.00
nitrogen			
$N_2(g)$	0	0	191.6
$N(g)$	472.704	455.5	153.3
$NO(g)$	90.25	87.6	210.8
$NO_2(g)$	33.2	51.30	240.1
$N_2O(g)$	81.6	103.7	220.0
$N_2O_3(g)$	83.72	139.41	312.17
$N_2O_4(g)$	11.1	99.8	304.4
$N_2O_5(g)$	11.3	115.1	355.7
$NH_3(g)$	–45.9	–16.5	192.8
$N_2H_4(l)$	50.63	149.43	121.21
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4NO_3(s)$	–365.56	–183.87	151.08
$NH_4Cl(s)$	–314.43	–202.87	94.6
$NH_4Br(s)$	–270.8	–175.2	113.0
$NH_4I(s)$	–201.4	–112.5	117.0
$NH_4NO_2(s)$	–256.5	—	—
$HNO_3(l)$	–174.1	–80.7	155.6
$HNO_3(g)$	–133.9	–73.5	266.9
oxygen			
$O_2(g)$	0	0	205.2
$O(g)$	249.17	231.7	161.1
$O_3(g)$	142.7	163.2	238.9
phosphorus			
$P_4(s)$	0	0	164.4
$P_4(g)$	58.91	24.4	280.0
$P(g)$	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.4
$P_4O_6(s)$	–1640.1	—	—
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$HPO_3(s)$	–948.5	—	—
$H_3PO_2(s)$	–604.6	—	—
$H_3PO_3(s)$	–964.4	—	—
$H_3PO_4(s)$	–1279.0	–1119.1	110.50
$H_3PO_4(l)$	–1266.9	–1124.3	110.5
$H_4P_2O_7(s)$	–2241.0	—	—
$POCl_3(l)$	–597.1	–520.8	222.5
$POCl_3(g)$	–558.5	–512.9	325.5
potassium			
$K(s)$	0	0	64.7
$K(g)$	89.0	60.5	160.3

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/K•mol)
potassium *continued*			
$KF(s)$	–576.27	–537.75	66.57
$KCl(s)$	–436.5	–408.5	82.6
silicon			
$Si(s)$	0	0	18.8
$Si(g)$	450.0	405.5	168.0
$SiO_2(s)$	–910.7	–856.3	41.5
$SiH_4(g)$	34.3	56.9	204.6
$H_2SiO_3(s)$	–1188.67	–1092.44	133.89
$H_4SiO_4(s)$	–1481.14	–1333.02	192.46
$SiF_4(g)$	–1615.0	–1572.8	282.8
$SiCl_4(l)$	–687.0	–619.8	239.7
$SiCl_4(g)$	–662.75	–622.58	330.62
SiC(*s, beta cubic*)	–73.22	–70.71	16.61
SiC(*s, alpha hexagonal*)	–71.55	–69.04	16.48
silver			
$Ag(s)$	0	0	42.55
$Ag(g)$	284.9	246.0	172.89
$Ag_2O(s)$	–31.05	–11.20	121.3
$AgCl(s)$	–127.0	–109.8	96.3
$Ag_2S(s)$	–32.6	–40.7	144.0
sodium			
$Na(s)$	0	0	51.3
$Na(g)$	107.5	77.0	153.7
$Na_2O(s)$	–414.2	–375.5	75.1
$NaCl(s)$	–411.2	–384.1	72.1
sulfur			
$S_8(s)$ (rhombic)	0	0	256.8
$S(g)$	278.81	238.25	167.82
$SO_2(g)$	–296.83	–300.1	248.2
$SO_3(g)$	–395.72	–371.06	256.76
$H_2S(g)$	–20.6	–33.4	205.8
$H_2SO_4(l)$	–813.989	690.00	156.90
$H_2S_2O_7(s)$	–1273.6	—	—
$SF_4(g)$	–728.43	–684.84	291.12
$SF_6(g)$	–1220.5	–1116.5	291.5
$SCl_2(l)$	–50	—	—
$SCl_2(g)$	–19.7	—	—
$S_2Cl_2(l)$	–59.4	—	—
$S_2Cl_2(g)$	–19.50	–29.25	319.45
$SOCl_2(g)$	–212.55	–198.32	309.66
$SOCl_2(l)$	–245.6	—	—
$SO_2Cl_2(l)$	–394.1	—	—
SO_2Cl_2(g)	–354.80	–310.45	311.83
tin			
$Sn(s)$	0	0	51.2
$Sn(g)$	301.2	266.2	168.5
$SnO(s)$	–285.8	–256.9	56.5
$SnO_2(s)$	–577.6	–515.8	49.0
$SnCl_4(l)$	–511.3	–440.1	258.6
$SnCl_4(g)$	–471.5	–432.2	365.8

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/K•mol)
titanium			
$\mathrm{Ti}(s)$	0	0	30.7
$\mathrm{Ti}(g)$	473.0	428.4	180.3
$\mathrm{TiO_2}(s)$	–944.0	–888.8	50.6
$\mathrm{TiCl_4}(l)$	–804.2	–737.2	252.4
$\mathrm{TiCl_4}(g)$	–763.2	–726.3	353.2
tungsten			
$\mathrm{W}(s)$	0	0	32.6
$\mathrm{W}(g)$	849.4	807.1	174.0
$\mathrm{WO_3}(s)$	–842.9	–764.0	75.9
zinc			
$\mathrm{Zn}(s)$	0	0	41.6
$\mathrm{Zn}(g)$	130.73	95.14	160.98
$\mathrm{ZnO}(s)$	–350.5	–320.5	43.7
$\mathrm{ZnCl_2}(s)$	–415.1	–369.43	111.5
$\mathrm{ZnS}(s)$	–206.0	–201.3	57.7
$\mathrm{ZnSO_4}(s)$	–982.8	–871.5	110.5
$\mathrm{ZnCO_3}(s)$	–812.78	–731.57	82.42
complexes			
cis-$[\mathrm{Co(NH_3)_4(NO_2)_2}]\mathrm{NO_3}$	–898.7	—	—
trans-$[\mathrm{Co(NH_3)_4(NO_2)_2}]\mathrm{NO_3}$	–896.2	—	—
$\mathrm{NH_4}[\mathrm{Co(NH_3)_2(NO_2)_4}]$	–837.6	—	—
$[\mathrm{Co(NH_3)_6}][\mathrm{Co(NH_3)_2(NO_2)_4}]_3$	–2733.0	—	—
cis-$[\mathrm{Co(NH_3)_4Cl_2}]\mathrm{Cl}$	–874.9	—	—
trans-$[\mathrm{Co(NH_3)_4Cl_2}]\mathrm{Cl}$	–877.4	—	—
cis-$[\mathrm{Co(en)_2(NO_2)_2}]\mathrm{NO_3}$	–689.5	—	—
cis-$[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$	–681.2	—	—
trans-$[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$	–677.4	—	—
$[\mathrm{Co(en)_3}](\mathrm{ClO_4})_3$	–762.7	—	—
$[\mathrm{Co(en)_3}]\mathrm{Br_2}$	–595.8	—	—
$[\mathrm{Co(en)_3}]\mathrm{I_2}$	–475.3	—	—
$[\mathrm{Co(en)_3}]\mathrm{I_3}$	–519.2	—	—
$[\mathrm{Co(NH_3)_6}](\mathrm{ClO_4})_3$	–1034.7	–221.1	615
$[\mathrm{Co(NH_3)_5NO_2}](\mathrm{NO_3})_2$	–1088.7	–412.9	331
$[\mathrm{Co(NH_3)_6}](\mathrm{NO_3})_3$	–1282.0	–524.5	448
$[\mathrm{Co(NH_3)_5Cl}]\mathrm{Cl_2}$	–1017.1	–582.5	366.1
$[\mathrm{Pt(NH_3)_4}]\mathrm{Cl_2}$	–725.5	—	—
$[\mathrm{Ni(NH_3)_6}]\mathrm{Cl_2}$	–994.1	—	—
$[\mathrm{Ni(NH_3)_6}]\mathrm{Br_2}$	–923.8	—	—
$[\mathrm{Ni(NH_3)_6}]\mathrm{I_2}$	–808.3	—	—

Standard Thermodynamic Properties for Selected Substances

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CH 223 Exam Prep II Worksheet Name: ____

Worksheet due dates: **Wed, 5/28: 9AM AC 1303** *(01)* **, 1:10 PM AC 2501** *(H1),* **11:59 PM** *(W1, email)*. Show ***detailed*** *steps* on how to get the given answer for each problem. *Failure to use this form for work and answers will result in a point penalty.*

Problem 1: How many grams of $Fe(OH)_2$ ($K_{sp} = 1.8 * 10^{-15}$) will dissolve in one liter of water buffered at pH = 12.00?

Answer to Problem #1: **$1.6 * 10^{-9}$ g**

Problem 2: Given that $\Delta G°_f$ for NH_3 = -16.67 kJ/mol, calculate the equilibrium constant for the following reaction at 298 K:

$$\mathbf{N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)}$$

Answer to Problem #2: **$6.98 * 10^5$**

<u>Problem 3</u>: Using the *unbalanced* reaction buffered at pH = 4.41 show below, determine the number of electrons transferred during the reaction. (Show the balanced reaction for credit!)

$$\mathbf{ClO_3^{-1}(aq) + I^{-1}(aq) \rightarrow I_2(g) + Cl_2(g)}$$

Answer to Problem #3: **Ten electrons are transferred.**

<u>Problem 4</u>: Determine ΔG° for a cell that utilizes the following reaction:

$$Cl_2(g) + 2\ Br^{-1}(aq) \rightarrow 2\ Cl^{-1}(aq) + Br_2(l)$$

The standard reduction for the chlorine is 1.360 V and the standard reduction for the bromine liquid is 1.077 V.

Answer to Problem #4: **-54.6 kJ**

<u>Problem 5</u>: If an electrolysis plant operates its electrolytic cells at a total current of 1.0 x 10^6 amp, how long will it take to produce one metric ton (one million grams) of Mg(s) from seawater containing Mg^{2+}?

Answer to Problem #5: **2.2 hours**

CH 223 Spring 2025:
Problem Set #6
Instructions

Step One (all sections):

- **Learn the material** for Problem Set #6 by **reading Chapter 18 and Chapter 19** of the textbook and/or by watching the videos found on our website (https://mhchem.org/223)
- **Try the problems** for Problem Set #6 found on the next pages on your own first. **Write out the answers (and show your work) by hand (on a tablet or paper)**; do not type your answers (and work) to avoid a point penalty. If you write the answers on the problem set itself, you will receive fewer points. Include your name on your problem set!

Step Two:

All sections: **Watch the recitation video** for Problem Set #6: **http://mhchem.org/v/x.htm**

Self correct *all* of the problems while viewing the video. Mark correct problems with a star (or other similar mark), and correct all incorrect problems (show the correct answer and the steps required to achieve it.) *Note* that Section 01 and Section H1 will not be going over this problem set in recitation.

Due dates:

- *Section 01:* due **Wednesday, June 4 at 9 AM in AC 1303**
- *Section H1:* due **Wednesday, June 4 at 1:10 PM in AC 2501**
- *Section W1:* Submit Problem Set #6 via **email (mike.russell@mhcc.edu)** as a single PDF file (use CamScanner (https://camscanner.com), CombinePDF (https://combinepdf.com), etc.) **by 11:59 PM Wednesday, June 4.**

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

CH 223 Problem Set #6

** Complete problem set on separate pieces of paper showing all work, circling final answers, etc.*
** Self correct your work before turning it in to the instructor.*

Covering: **Chapters Eighteen** *and* **Chapter Nineteen** *and* **Chapter Guide Six**
Important Tables and/or Constants: "**Coordination Compounds**" *(Handout)*

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1. Write an equation for the reaction of potassium and hydrogen. Name the product. Is it ionic or covalent? Predict one physical property and one chemical property of this compound.
2. Write an equation for the reaction of sodium with each of the halogens. Predict at least two physical properties that are common to all of the alkali metal halides.
3. $Ca(OH)_2$ has a K_{sp} of 5.5×10^{-5}, whereas K_{sp} for $Mg(OH)_2$ is 5.6×10^{-12}. Calculate the equilibrium constant for the reaction:

   $$Ca(OH)_2(s) + Mg^{2+}(aq) \rightleftharpoons Ca^{2+}(aq) + Mg(OH)_2(s)$$

   Explain why this reaction can be used in the commercial isolation of magnesium from seawater.
4. Gallium hydroxide, like aluminum hydroxide, is amphoteric
   a. Write balanced equations for the reaction of solid $Ga(OH)_3$ with aqueous HCl and NaOH.
   b. What volume of 0.0112 M HCl is needed to react completely with 1.25 g of $Ga(OH)_3$?
5. Use data in the Thermodynamic Table in Problem Set #5 to calculate the enthalpy and free energy change for the reaction: $2\ NO_2(g) \rightarrow N_2O_4(g)$
   Is this reaction exothermic or endothermic? Is the reaction product- or reactant-favored?
6. The overall reaction involved in the industrial synthesis of nitric acid is:

   $$NH_3(g) + 2\ O_2(g) \rightarrow HNO_3(aq) + H_2O(\ell)$$

   a. Calculate $\Delta G°$ for this reaction. *Note:* $\Delta G°$ for $HNO_3(aq) = -111.25$ kJ/mol
   b. Calculate the equilibrium constant for this reaction at 25 °C.
7. Sulfur forms a range of compounds with fluorine. Draw Lewis electron dot structures for S_2F_2 (connectivity is FSSF), SF_2, SF_4, SF_6 and S_2F_{10}. What is the oxidation number of sulfur in each of these compounds?
8. The halogen oxides and oxoanions are good oxidizing agents. For example, the reduction of bromate ion has an $E°$ value of 1.44 V in acid solution:

   $$2\ BrO_3^{-1}(aq) + 12\ H^+(aq) + 10\ e^- \rightarrow Br_2(aq) + 6\ H_2O(\ell)$$

   Is it possible to oxidize aqueous 1.0 M Mn^{2+} to aqueous MnO_4^{-1} with 1.0 M bromate ion? *Use the redox table in Problem Set #5 to answer this problem.*
9. The hypohalite ions, XO^{-1}, are the anions of weak acids. Calculate the pH of a 0.10 M solution of NaClO. What is the concentration of HClO in this solution? $K_b\ (ClO^-) = 2.9 * 10^{-7}$
10. Identify two transition metals ions with the following electron configurations:
    a. $[Ar]3d^6$
    b. $[Ar]3d^{10}$
    c. $[Ar]3d^5$
    d. $[Ar]3d^8$
11. Match up the isoelectronic ions in the following list:

    $$Cu^+\ \ Mn^{2+}\ \ Fe^{2+}\ \ Co^{3+}\ \ Fe^{3+}\ \ Zn^{2+}\ \ Ti^{2+}\ \ V^{3+}$$

Problem Set #6 continues on the next page

12. Identify the products of each reaction and balance the equation:
    a. $CuSO_4(aq) + Zn(s) \rightarrow$
    b. $Zn(s) + HCl(aq) \rightarrow$
13. One of the following nitrogen compounds or ions is not capable of serving as a ligand: NH_4^+, NH_3, NH_2^{-1}. Identify this species and explain your answer.
14. Give the oxidation number of the metal in each of the following complexes:
    a. $[Fe(NH_3)_6]^{2+}$
    b. $[Zn(CN)_4]^{2-}$
    c. $[Co(NH_3)_5(NO_2)]^+$
    d. $[Cu(en)_2]^{2+}$
15. Give the formula of a complex constructed from one Cr^{3+} ion, two ethylenediamine ligands, and two ammonia molecules. Is the complex neutral or is it charged? If charged, give the charge.
16. Write formulas for the following ions or compounds:
    a. diamminetriaquahydroxochromium(II) nitrate
    b. hexaammineiron(III) nitrate
    c. pentacarbonyliron(0) (where the ligand is CO)
    d. ammonium tetrachlorocuprate(II)
17. Name the following ions or compounds:
    a. $[Co(H_2O)_4Cl_2]^+$
    b. $Co(H_2O)_3F_3$
    c. $[Pt(NH_3)Br_3]^{-1}$
    d. $[Co(en)(NH_3)_3Cl]^{2+}$
18. Give the name or formula for each ion or compound as appropriate:
    a. tetraaquadichlorochromium(III) chloride
    b. $[Cr(NH_3)_5SO_4]Cl$
    c. sodium tetrachlorocobaltate(II)
    d. *trans*-diaquadioxalatochromate(III) ion (oxalato = oxalate ion)
    e. $[Rh(en)_3]^{3+}$
19. In which of the following complexes are geometric isomers possible? If isomers are possible, draw their structures and label them as *cis* or *trans*, or as *fac* or *mer*.
    a. $[Co(H_2O)_4Cl_2]^+$
    b. $Co(NH_3)_3F_3$
    c. $[Pt(NH_3)Br_3]^{-1}$
    d. $[Co(en)_2(NH_3)Cl]^{2+}$
    e. Does 2-butanol exhibit optical isomerism? Draw a Lewis structure and explain.
20. A platinum-containing compound, known as Magnus's green salt, has the overall formula $[Pt(NH_3)_4][PtCl_4]$ (in which both platinum ions are Pt^{2+}). Name the cation and the anion.

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CH 223 Final Exam Prep Worksheet Name: ____________________

Worksheet due dates: **<u>Wed, 6/4</u>: 9AM AC 1303** *(01)* **, 1:10 PM AC 2501** *(H1),* **11:59 PM** *(W1, email)*. Show ***detailed*** *steps* on how to get the given answer for each problem. *Failure to use this form for work and answers will result in a point penalty.*

Problem 1: Lauryl alcohol is obtained from coconut oil and is used to make detergents. A solution of 5.00 g of lauryl alcohol in 100. grams of benzene freezes at 4.1 °C. What is the molar mass of lauryl alcohol? (for benzene, k_{fp} = 5.12 °C/m; normal freezing point of benzene = 5.5 °C)

Answer to Problem #1: **180 g/mol**

Problem 2: Rubidium has an atomic weight of 85.470 and two primary isotopes, namely rubidium-85 (84.9118 amu) and rubidium-87 (86.9092 amu). Calculate the abundance of each isotope.

Answer to Problem #2: **^{85}Rb = 72.05%, ^{87}Rb = 27.95%**

Problem 3: Determine both the molecular and net ionic equations for the following reactions. *To get credit for this problem, both equations must be listed for each problem, and all states of matter (and charges) provided.*

a. Lead(II) nitrate is mixed with sodium iodide.

Molecular (balanced) equation:

Net ionic equation:

b. Aqueous strontium hydroxide is mixed with chromium(III) chloride.

Molecular (balanced) equation:

Net ionic equation:

Hints for Problem #3: a. **$PbI_2(s)$** *and b.* **$Cr(OH)_3(s)$**

Problem 4: *Three pH problems:*

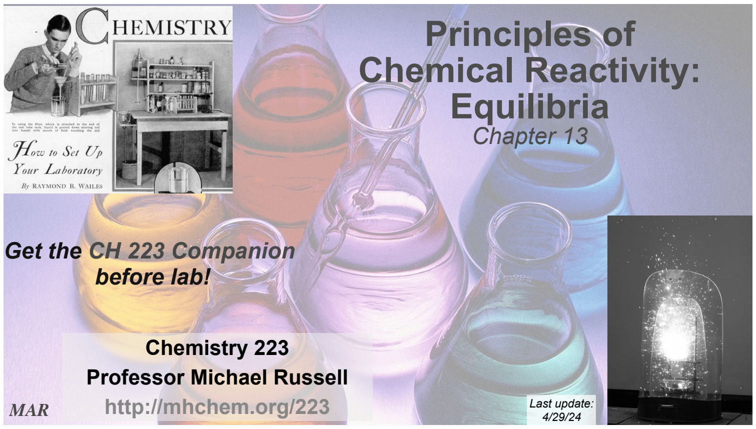
Calculate the pH of a 0.200 M NaOH solution.	Calculate the pH of a 0.200 M acetic acid solution. $K_a = 1.8 \times 10^{-5}$	Calculate the pH of a solution containing 220. mL of 0.115 M pyridine ($K_b = 1.4 \times 10^{-9}$) and 150. mL of 0.100 M HCl.
pH = ________________	pH = ________________	pH = ________________

Answer to Problem #4: **13.301, 2.72 and 4.99** *(4.98 ok)*

Problem 5: Determine the rate law for the following reaction and the value of the rate constant, *k*. **$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$**

Experiment	**[NO] (M)**	**$[O_2]$ (M)**	**Rate (M/s)**
1	0.0126	0.0125	1.41×10^{-2}
2	0.0252	0.0125	5.64×10^{-2}
3	0.0252	0.0250	1.13×10^{-1}

Answer to Problem #5: **rate = $k[NO]^2[O_2]$, $k = 7.11 \times 10^3$** *(7.12×10^3 ok)*



Principles of Chemical Reactivity: Equilibria

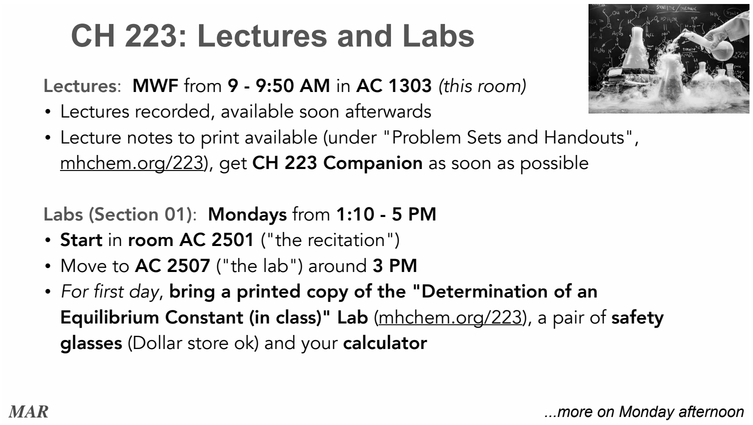
Chapter 13

Get the CH 223 Companion before lab!

Chemistry 223
Professor Michael Russell
http://mhchem.org/223

MAR

Last update: 4/29/24



CH 223: Lectures and Labs

Lectures: **MWF** from **9 - 9:50 AM** in **AC 1303** *(this room)*

- Lectures recorded, available soon afterwards
- Lecture notes to print available (under "Problem Sets and Handouts", mhchem.org/223), get **CH 223 Companion** as soon as possible

Labs (Section 01): **Mondays** from **1:10 - 5 PM**

- **Start** in **room AC 2501** ("the recitation")
- Move to **AC 2507** ("the lab") around **3 PM**
- *For first day*, **bring a printed copy of the "Determination of an Equilibrium Constant (in class)" Lab** (mhchem.org/223), a pair of **safety glasses** (Dollar store ok) and your **calculator**

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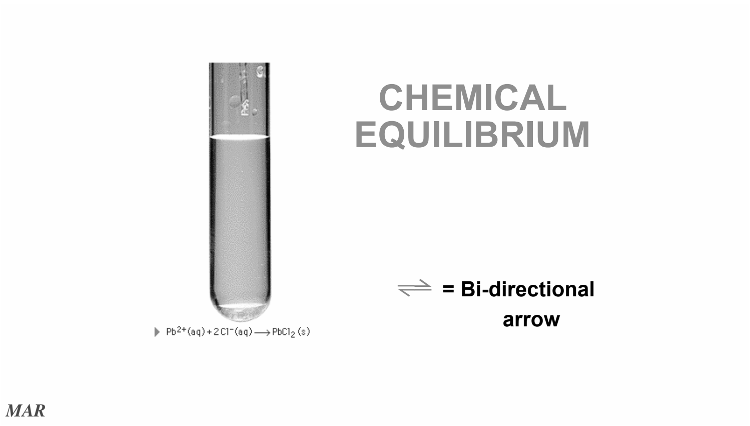
...more on Monday afternoon



$Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$

CHEMICAL EQUILIBRIUM

$\rightleftharpoons$ = **Bi-directional arrow**

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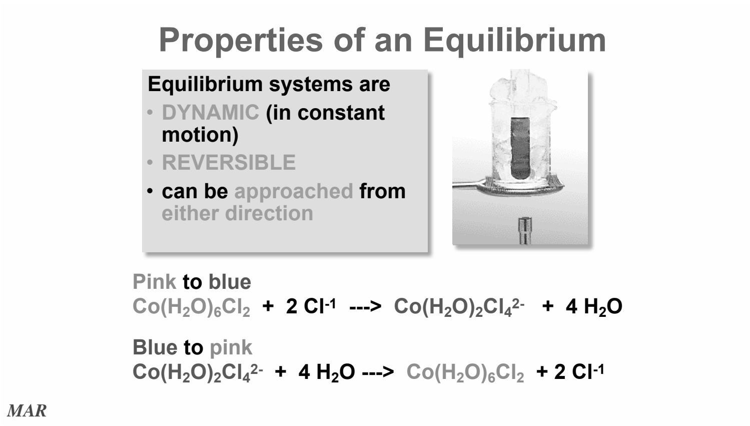

Properties of an Equilibrium

Equilibrium systems are

- **DYNAMIC (in constant motion)**
- **REVERSIBLE**
- **can be approached from either direction**

Pink to blue
$Co(H_2O)_6Cl_2 + 2 Cl^{-1} \text{ ---> } Co(H_2O)_2Cl_4^{2-} + 4 H_2O$

Blue to pink
$Co(H_2O)_2Cl_4^{2-} + 4 H_2O \text{ ---> } Co(H_2O)_6Cl_2 + 2 Cl^{-1}$

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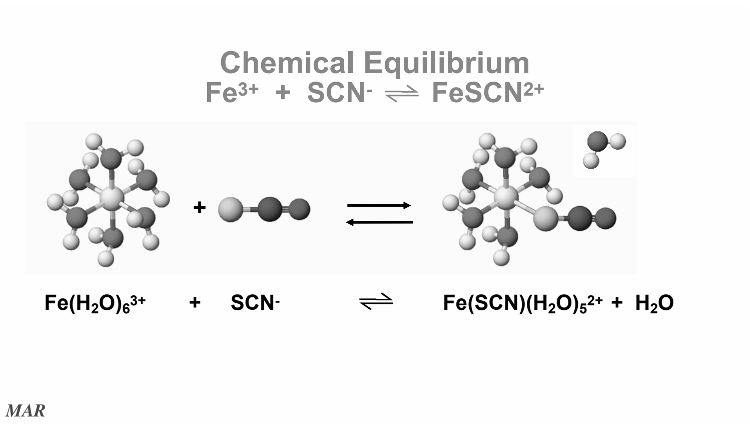
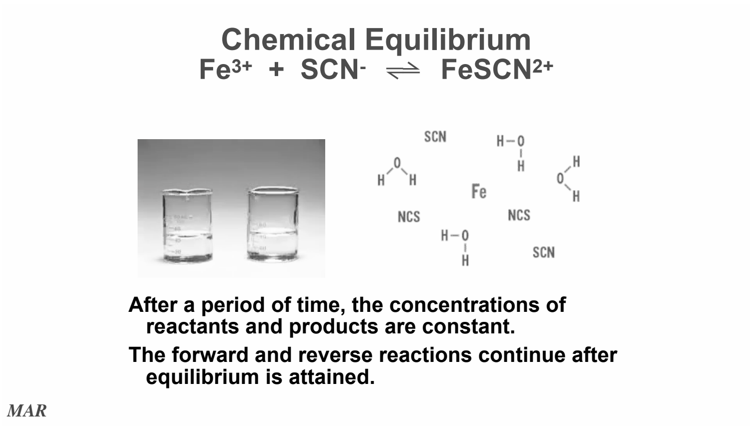


Chemical Equilibrium

$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$

$Fe(H_2O)_6^{3+} + SCN^- \rightleftharpoons Fe(SCN)(H_2O)_5^{2+} + H_2O$

MAR



Chemical Equilibrium

$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$

After a period of time, the concentrations of reactants and products are constant.

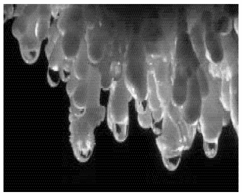
The forward and reverse reactions continue after equilibrium is attained.

MAR

Phase changes:

$H_2O(s) \rightleftharpoons H_2O(liq)$

Examples of Chemical Equilibria



Formation of stalactites and stalagmites:

$CaCO_3(s) + H_2O(liq) + CO_2(g) \rightleftharpoons$

$Ca^{2+}(aq) + 2\ HCO_3^-(aq)$

The Equilibrium Constant

For any type of chemical equilibrium of the type

$a\,A + b\,B \rightleftharpoons c\,C + d\,D$

the following is a CONSTANT (at a *given T*)

conc. of products

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

conc. of reactants

equilibrium constant

If K is known, we can predict concentrations of products or reactants.

MAR

The Equilibrium Constant: Example

Equilibrium constants, K, come from *kinetic rate constants, k*

Example: **For $2\ NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$,**

$rate_f = k_f[NO_2]^2$

$rate_r = k_r[N_2O_4]$

When rates equal, $rate_f = rate_r$, and

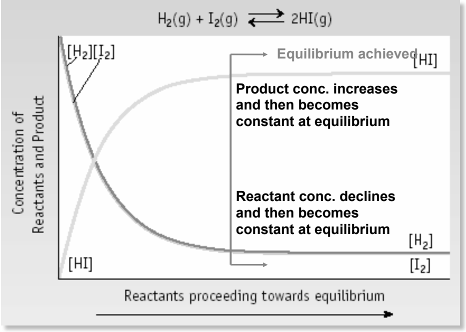
$k_f[NO_2]^2 = k_r[N_2O_4]$

$[N_2O_4]/[NO_2]^2 = k_f/k_r = K$ *(equilibrium)*

Product of two constants (k_f & k_r) is itself a constant (K)!

MAR

The Equilibrium Constant: Example



Product conc. increases and then becomes constant at equilibrium

Reactant conc. declines and then becomes constant at equilibrium

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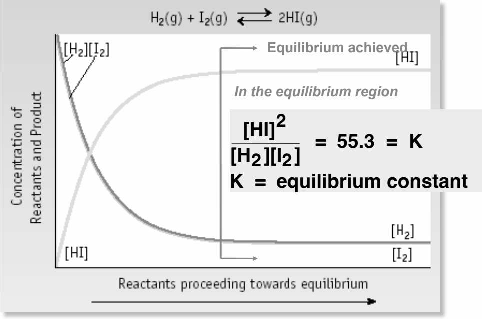
The Equilibrium Constant: Example



In the equilibrium region

$$\frac{[HI]^2}{[H_2][I_2]} = 55.3 = K$$

K = equilibrium constant

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Determining K

$2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$

Place 2.00 mol of NOCl is a 1.00 L flask. At equilibrium you find 0.66 mol/L of NO. Calculate K.

Solution

Set of a table of concentrations (ICE)

	[NOCl]	[NO]	[Cl_2]
Initial	2.00	0	0
Change			
Equilibrium		**0.66**	

MAR

Determining K

$2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$

Place 2.00 mol of NOCl is a 1.00 L flask. At equilibrium you find 0.66 mol/L of NO. Calculate K.

Solution

Set of a table of concentrations (ICE)

	[NOCl]	[NO]	[Cl_2]
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33
Equilibrium	1.34	0.66	0.33

How to remember ICE:

MAR

Determining K

$2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$

	[NOCl]	[NO]	[Cl_2]
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33
Equilibrium	1.34	0.66	0.33

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.66)^2(0.33)}{(1.34)^2} = 0.080$$

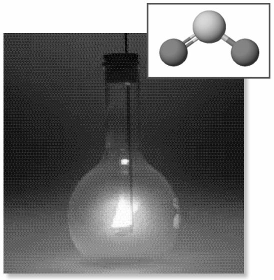
MAR

Writing and Manipulating K Expressions

Solids and liquids *NEVER* appear in equilibrium expressions.

$S(s) + O_2(g) \rightleftharpoons SO_2(g)$

$$K = \frac{[SO_2]}{[O_2]}$$



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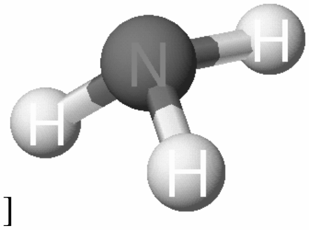
Writing and Manipulating K Expressions

Solids and liquids *NEVER* appear in equilibrium expressions.

$NH_3(aq) + H_2O(liq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$



$$K = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

MAR

Writing and Manipulating K Expressions

Adding equations for reactions

$S(s) + O_2(g) \rightleftharpoons SO_2(g) \quad K_1 = [SO_2] / [O_2]$

$SO_2(g) + 1/2\ O_2(g) \rightleftharpoons SO_3(g)$

$K_2 = [SO_3] / [SO_2][O_2]^{1/2}$

NET EQUATION

$S(s) + 3/2\ O_2(g) \rightleftharpoons SO_3(g)$

$$K_{net} = \frac{[SO_3]}{[O_2]^{3/2}} = K_1 \bullet K_2$$

MAR

Writing and Manipulating K Expressions

Changing coefficients

$S(s) + 3/2\ O_2(g) \rightleftharpoons SO_3(g)$ $\quad K_{old} = \frac{[SO_3]}{[O_2]^{3/2}}$

$2\ S(s) + 3\ O_2(g) \rightleftharpoons 2\ SO_3(g)$

$$K_{new} = \frac{[SO_3]^2}{[O_2]^3}$$

$$K_{new} = \frac{[SO_3]^2}{[O_2]^3} = (K_{old})^2$$

MAR

Writing and Manipulating K Expressions

Changing direction

$S(s) + O_2(g) \rightleftharpoons SO_2(g)$ $$K = \frac{[SO_2]}{[O_2]}$$

$SO_2(g) \rightleftharpoons S(s) + O_2(g)$ $$K_{new} = \frac{[O_2]}{[SO_2]}$$

and: $$K_{new} = \frac{[O_2]}{[SO_2]} = \frac{1}{K_{old}}$$

See Manipulating Equilibrium Constant Expressions

MAR

Kp Expressions

We have been writing K in terms of M (mol/L), designated by K_c

Equilibrium constants expressed in terms of gases designated K_p where all pressures in atm *(760 mm Hg = 1 atm)*

For: $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad K_p = \frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}}$$

MAR

Converting K_c Into K_p

$$K_p = K_c(RT)^{\Delta n}$$

T = Temperature (K)

$R = 0.082057$ L atm mol^{-1} K^{-1}

Δn = change in moles of gas

Example:

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

$\Delta n = 2 - 4 = -2$

see: Types of Equilibrium Constants

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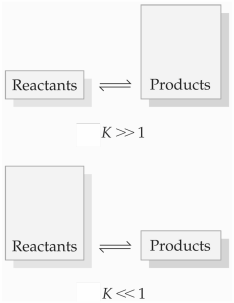
The Meaning of K



If *K*>>1, the reaction is *product-favored*; product predominates at equilibrium.

If *K*<<1, the reaction is *reactant-favored*; reactant predominates at equilibrium.

MAR

The Meaning of K

Can tell if a reaction is product-favored or reactant-favored.

For: $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 3.5 \text{ x } 10^8$$

Conc. of products is much greater than that of reactants at equilibrium.

The reaction is strongly product-favored.

MAR

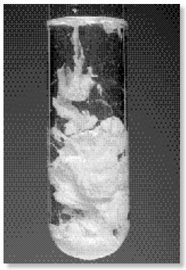
The Meaning of K

For: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$K_c = [Ag^+]\ [Cl^-] = 1.8 \text{ x } 10^{-5}$

Conc. of products is much less than that of reactants at equilibrium.

The reaction is strongly reactant-favored.



The reverse reaction
$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$
*is **product-favored,***

$K_{rev} = 1/1.8 \text{ x } 10^{-5} = 5.6 \text{ x } 10^4$

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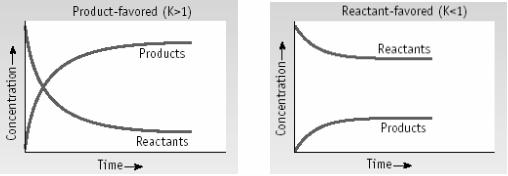
Product- or Reactant Favored



Product-favored
K > 1

Reactant-favored
K < 1

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The Reaction Quotient, Q

All reacting chemical systems can be characterized by their REACTION QUOTIENT, Q.

For: **$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$**

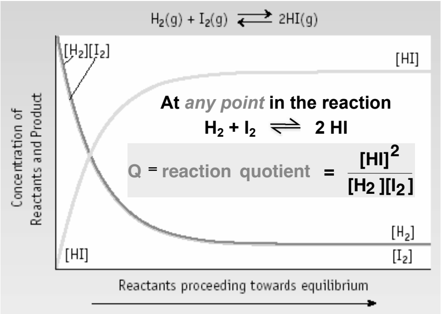
Under Any Reaction Conditions

$$\text{Reaction quotient} = Q = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \quad \begin{matrix}\text{Product concentrations}\\ \text{Reactant concentrations}\end{matrix}$$

If Q = K, then system is at equilibrium.
If Q ≠ K, then system is not at equilibrium

MAR

The Reaction Quotient, Q



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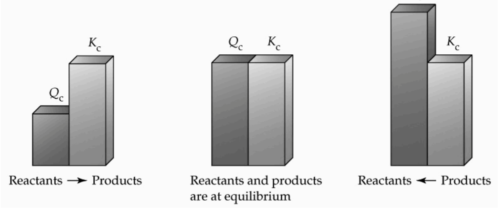
The Reaction Quotient, Q

Comparing Q and K:

Q < K, **reaction** shifts to the products (right)

Q > K, **reaction** shifts to the reactants (left)

Q = K, **reaction is** at equilibrium



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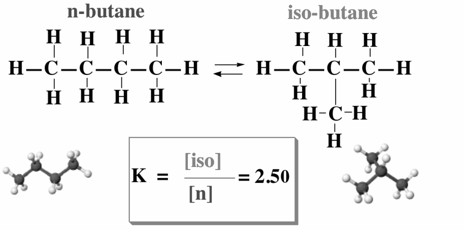
The Reaction Quotient, Q

We can use Q to tell if a reaction is at equilibrium. If not at equilibrium, we can predict which way the reaction will move to approach equilibrium.

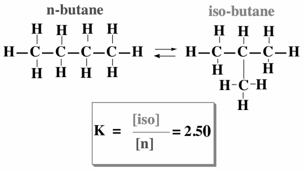


$$K = \frac{[\text{iso}]}{[\text{n}]} = 2.50$$

see Understanding K and Q Handout

MAR

The Reaction Quotient, Q



$$K = \frac{[\text{iso}]}{[\text{n}]} = 2.50$$

If [iso] = 0.35 M and [n] = 0.15 M, are you at equilibrium?

Which way does the reaction "shift" to approach equilibrium?

$$Q = \frac{\text{conc. of iso}}{\text{conc. of n}} = \frac{0.35}{0.15} = 2.3$$

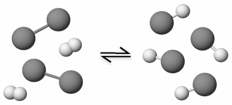
To [iso]! Q = 2.3, Q < K, reaction will shift to "right" (product side, or [iso])

MAR

Typical Calculations

$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 55.3$$



Place 1.00 mol each of H_2 and I_2 in a 1.00 L flask. Calc. equilibrium concentrations.

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$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$, K_c = 55.3

Step 1. Set up ICE table to define EQUILIBRIUM concentrations.

	$[H_2]$	$[I_2]$	$[HI]$
Initial			
Change			
Equilib			

where x is defined as am't of H_2 and I_2 consumed on approaching equilibrium.

MAR

$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$, K_c = 55.3

Step 2. Put equilibrium concentrations into K_c expression.

$$K_c = \frac{[2x]^2}{[1.00\text{-}x][1.00\text{-}x]} = 55.3$$

MAR

$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$, K_c = 55.3

Step 3. Solve K_c expression - take square root of both sides.

$$7.44 = \frac{2x}{1.00 - x}$$

7.44 (1.00 - x) = 2x

7.44 - 7.44x = 2x

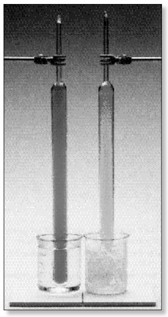
x = 7.44 / 9.44 = 0.788

Therefore, at equilibrium

$[H_2]$ = $[I_2]$ = 1.00 - x = 0.21 M

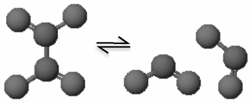
$[HI]$ = 2x = 1.58 M

MAR



Nitrogen Dioxide Equilibrium

$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$



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Nitrogen Dioxide Equilibrium
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.0059 \text{ at } 298\text{ K}$$

If initial concentration of N_2O_4 is 0.50 M, what are the equilibrium concentrations?

Step 1. Set up an equilibrium table

	$[N_2O_4]$	$[NO_2]$
Initial	0.50	0
Change		
Equilib		

MAR

Nitrogen Dioxide Equilibrium
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.0059 \text{ at } 298 \text{ K}$$

If initial concentration of N_2O_4 is 0.50 M, what are the equilibrium concentrations?

Step 1. Set up an equilibrium table

	$[N_2O_4]$	$[NO_2]$
Initial	0.50	0
Change	-x	+2x
Equilib	0.50 - x	2x

MAR

Nitrogen Dioxide Equilibrium
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

Step 2. Substitute into K_c expression and solve.

$$K_c = 0.0059 = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{(0.50 - x)}$$

Rearrange:

$$0.0059\ (0.50 - x) = 4x^2$$
$$0.0029 - 0.0059x = 4x^2$$
$$4x^2 + 0.0059x - 0.0029 = 0$$

This is a QUADRATIC EQUATION

$ax^2 + bx + c = 0$

$a = 4 \quad b = 0.0059 \quad c = -0.0029$

*CH 223: report **both** values of x when performing quadratic calculations*

MAR

Nitrogen Dioxide Equilibrium
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

Solve the quadratic equation for x.

$ax^2 + bx + c = 0$

$a = 4 \quad b = 0.0059 \quad c = -0.0029$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.0059 \pm \sqrt{(0.0059)^2 - 4(4)(-0.0029)}}{2(4)}$$

$$x = -0.00074 \pm 1/8(0.046)^{1/2} = -0.00074 \pm 0.027$$

MAR

Nitrogen Dioxide Equilibrium
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

$$x = \frac{-0.0059 \pm \sqrt{(0.0059)^2 - 4(4)(-0.0029)}}{2(4)}$$

$$x = -0.00074 \pm 1/8(0.046)^{1/2} = -0.00074 \pm 0.027$$

$x = 0.026$ or -0.028

But a *negative* value is not reasonable.

***Conclusion:* x = 0.026**

$[N_2O_4] = 0.50 - x = 0.47$ M

$[NO_2] = 2x = 0.052$ M

*CH 223: report **both** values of x when performing quadratic calculations*

MAR

Le Chatelier's Principle

Temperature, changes in volume, changes in pressure and changes in concentration affect equilibria.

The outcome is governed by LE CHATELIER'S PRINCIPLE

"...if a system at equilibrium is disturbed, the system tends to shift its equilibrium position to counter the effect of the disturbance."

Henri Le Chatelier, 1850 - 1936

MAR

Temperature effects change the numeric value of K

Consider the fizz in a soft drink

$CO_2(g) + H_2O(liq) \rightleftharpoons CO_2(aq) +$ heat

Decrease T. *What happens to equilibrium position? To value of K?*

K = $[CO_2]$ / P (CO_2)

K *increases* as T goes down because $[CO_2]$ increases *and* P(CO_2) decreases.

Increase T. *Now what?*

Equilibrium shifts left *and* K *decreases*.

see: Le Chatelier's Guide

MAR

Temperature Effects on Equilibrium

N_2O_4 (colorless) + heat $\rightleftharpoons$ 2 NO_2 (brown)

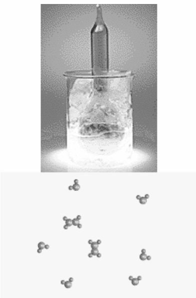
ΔH^o = + 57.2 kJ *(endothermic)*

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

K_c = 0.00077 at 273 K

K_c = 0.0059 at 298 K

K changes with temperature



MAR

Volume & Pressure Effects on Equilibrium

$N_2O_4(g)$ + heat $\rightleftharpoons$ 2 $NO_2(g)$

colorless gas *brown gas*

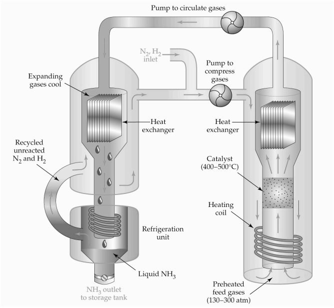
endothermic

Volume and Pressure changes affect equilibrium

Larger volume / Less Pressure = more molecules

Smaller volume / Higher Pressure = fewer molecules

MAR



NH_3 Production

Catalyst for the Haber-Frisch reaction is mostly Fe with some KOH

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

K = 3.5×10^8 at 298 K

MAR

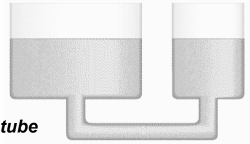
EQUILIBRIUM AND EXTERNAL EFFECTS

***Concentration changes* ---> no change in K - only the *position* of equilibrium changes.**

We can use the "water U-tube" to demonstrate this phenomena (and connect to Haber-Frisch)

Haber-Frisch reaction:

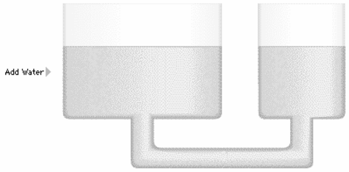
$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$



Water U-tube

MAR

Le Chatelier's Principle



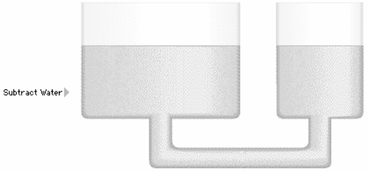
Adding a "reactant" to a chemical system.

Haber-Frisch reaction: adding N_2 or H_2, reaction moves to right

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

MAR

Le Chatelier's Principle



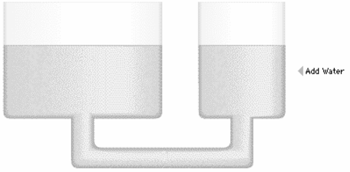
Removing a "reactant" from a chemical system.

Haber-Frisch reaction: removing N_2 or H_2, reaction moves to left

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

MAR

Le Chatelier's Principle



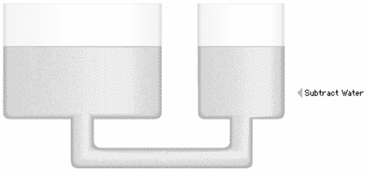
Adding a "product" to a chemical system.

Haber-Frisch reaction: adding NH_3,
reaction moves to left

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

MAR

Le Chatelier's Principle

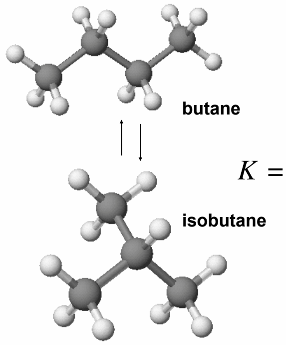


Removing a "product" from a chemical system.

Haber-Frisch reaction: removing NH_3,
reaction moves to right

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

MAR



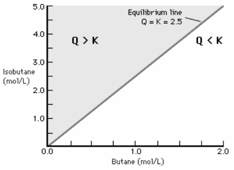
Butane-Isobutane Equilibrium

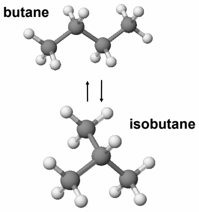
$$K = \frac{[\text{isobutane}]}{[\text{butane}]} = 2.50$$

MAR

Butane $\rightleftharpoons$ Isobutane

Assume you are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane. When the system comes to equilibrium again, what are [iso] and [butane]? K = 2.50





MAR

Butane $\rightleftharpoons$ Isobutane

Assume you are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane. When the system comes to equilibrium again, what are [iso] and [butane]? K = 2.50

Solution

Calculate Q immediately after adding more butane and compare with K.

$$Q = \frac{[\text{isobutane}]}{[\text{butane}]} = \frac{1.25}{0.50 + 1.50} = 0.625$$

Q is *LESS THAN* K. Therefore, the reaction will shift to the ____________.

MAR

Butane $\rightleftharpoons$ Isobutane

You are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane.

Solution

Q is less than K, so equilibrium shifts right - away from butane and toward isobutane.

Set up concentration (ICE) table

	[butane]	**[isobutane]**
Initial		
Change		
Equilibrium		

MAR

Butane $\rightleftharpoons$ Isobutane

You are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane.

Solution

$$K = 2.50 = \frac{[\text{isobutane}]}{[\text{butane}]} = \frac{1.25 + x}{2.00 - x}$$

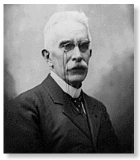
x = 1.07 M

At the new equilibrium position,

[butane] = 0.93 M and [isobutane] = 2.32 M

Equilibrium has shifted toward isobutane.

MAR



Le Chatelier's Principle - Overview

Change T

- **changes the value of K**
- **changes observed in P, V or concentrations at equilibrium**

Add or take away reactant or product

- **K does not change**
- **Reaction adjusts to new equilibrium "position"**

Use a catalyst

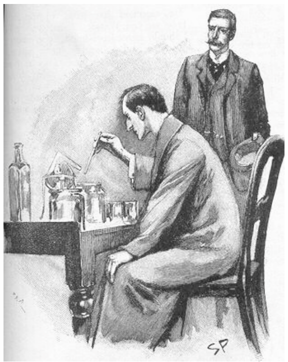
- **reaction comes more quickly to equilibrium. K not changed.**

MAR

End of Chapter 13

See:

- *Chapter Thirteen Study Guide*
- *Chapter Thirteen Concept Guide*
- *Types of Equilibrium Constants*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*



MAR

Important Equations, Constants, and Handouts from this Chapter:

for: a A + b B $\rightleftharpoons$ c C + d D

$$\underset{\text{equilibrium constant}}{\mathbf{K}} = \frac{\overset{\text{conc. of products}}{[C]^c\,[D]^d}}{\underset{\text{conc. of reactants}}{[A]^a\,[B]^b}}$$

$K_p = K_c(RT)^{\Delta n}$

R = 0.082057 L atm mol^{-1} K^{-1}

Under Any Reaction Conditions

$$\text{Reaction quotient} = Q = \frac{\overset{\text{Product concentrations}}{[C]^c[D]^d}}{\underset{\text{Reactant concentrations}}{[A]^a[B]^b}}$$

Handouts:

- *Manipulating Equilibrium Constant Expressions*
- *Types of Equilibrium Constants*

Le Chatelier's Principle

MAR

End of Chapter Problems: *Test Yourself*

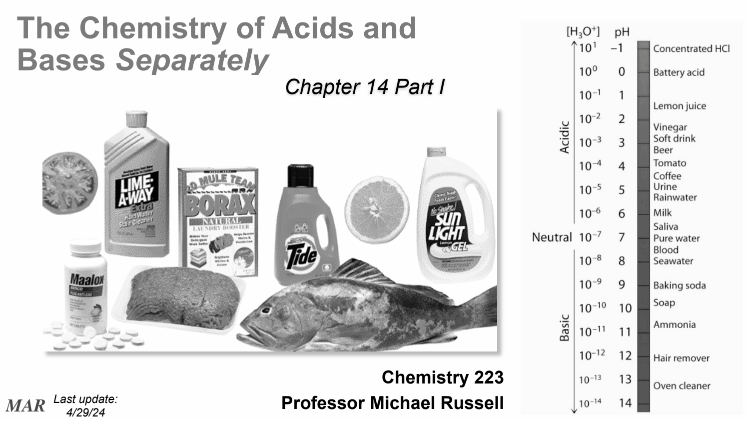
1. Write an equilibrium constant expression for the following reaction: C(s) + CO_2(g) $\rightleftarrows$ 2 CO(g)
2. K = 5.6 x 10^{-12} at 500 K for the dissociation of iodine molecules to iodine atoms: **I_2(g) $\rightleftarrows$ 2 I(g)** A mixture has [I_2] = 0.020 mol/L and [I] = 2.0 x 10^{-8} mol/L. Is the reaction at equilibrium (at 500 K)? If not, which way must the reaction proceed to reach equilibrium?
3. The reaction: PCl_5(g) $\rightleftarrows$ PCl_3(g) + Cl_2(g) was examined at 250 °C. At equilibrium, [PCl_5] = 4.2 x 10^{-5} mol/L, [PCl_3] = 1.3 x 10^{-2} mol/L, and [Cl_2] = 3.9 x 10^{-3} mol/L. Calculate K for the reaction.
4. The equilibrium constant for the dissociation of iodine molecules to iodine atoms: **I_2(g) $\rightleftarrows$ 2 I(g)** is 3.76 x 10^{-3} at 1000 K. Suppose 0.105 mol of I_2 is placed in a 12.3 L flask at 1000 K. What are the concentrations of I_2 and I when the system comes to equilibrium?
5. Dinitrogen trioxide decomposes to NO and NO_2 in an endothermic process (ΔH = 40.5 kJ/mol): **N_2O_3(g) $\rightleftarrows$ NO(g) + NO_2(g)** Predict the effect of the following changes on the position of the equilibrium (left, right, or no change):
   a. adding more N_2O_3(g)
   b. adding more NO_2(g)
   c. increasing the volume of the reaction flask
   d. lowering the temperature

MAR

End of Chapter Problems: *Answers*

1. $K_c = [CO]^2 / [CO_2]$ or $K_p = P_{CO}{}^2 / P_{CO2}$
2. No, Q < K, reaction will proceed to the right (more products)
3. K = 1.2
4. [I_2] = 0.00614 M, [I] = 0.00480 M
5. a. right b. left c. right d. left

MAR

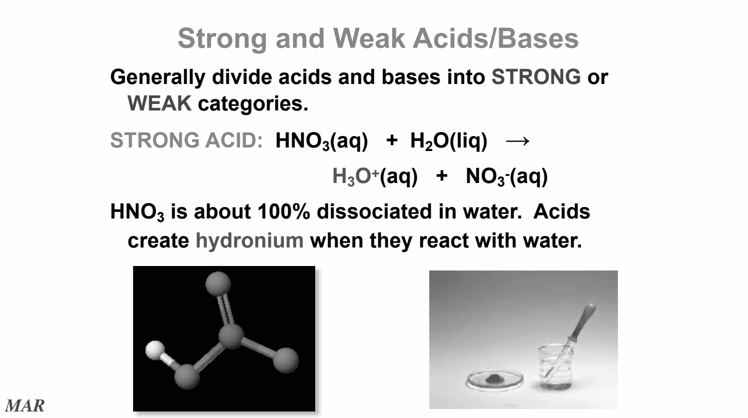


The Chemistry of Acids and Bases *Separately*

Chapter 14 Part I

Chemistry 223
Professor Michael Russell

MAR *Last update: 4/29/24*



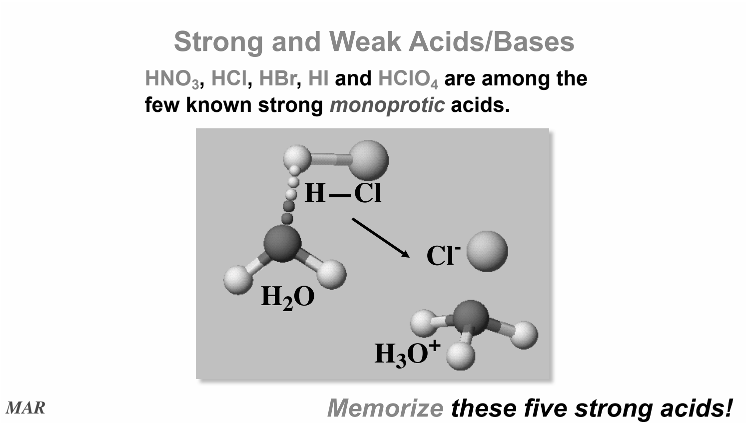
Strong and Weak Acids/Bases

Generally divide acids and bases into STRONG or WEAK categories.

STRONG ACID: $HNO_3(aq) + H_2O(liq) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

HNO_3 is about 100% dissociated in water. Acids create hydronium when they react with water.

MAR

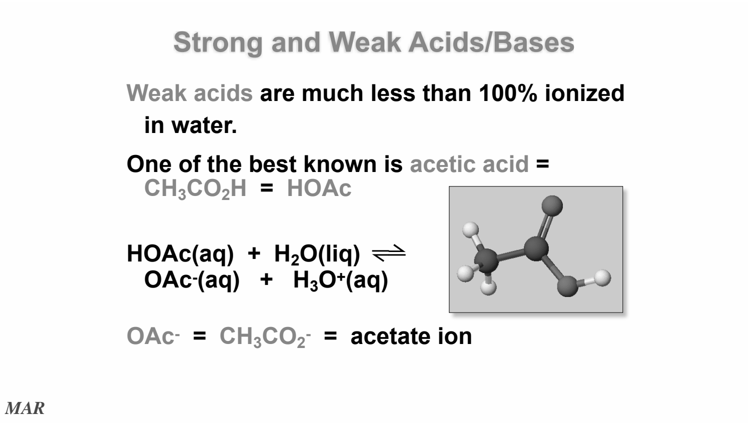


Strong and Weak Acids/Bases

HNO_3, HCl, HBr, HI and $HClO_4$ are among the few known strong *monoprotic* acids.

MAR

Memorize these five strong acids!



Strong and Weak Acids/Bases

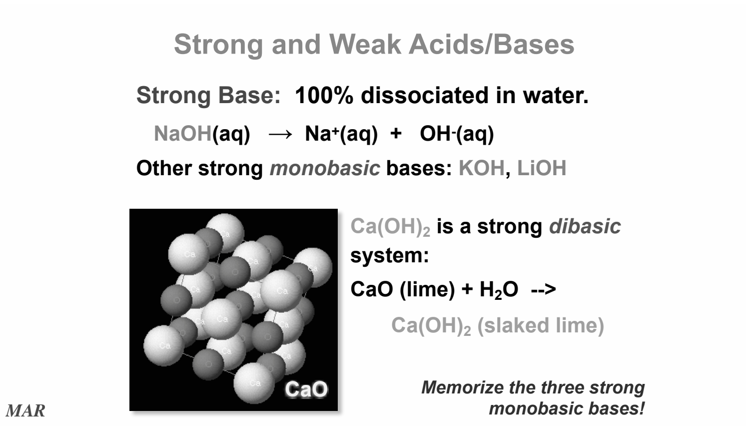
Weak acids are much less than 100% ionized in water.

One of the best known is acetic acid = CH_3CO_2H = HOAc

$HOAc(aq) + H_2O(liq) \rightleftharpoons OAc^-(aq) + H_3O^+(aq)$

OAc^- = $CH_3CO_2^-$ = acetate ion

MAR



Strong and Weak Acids/Bases

Strong Base: 100% dissociated in water.

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

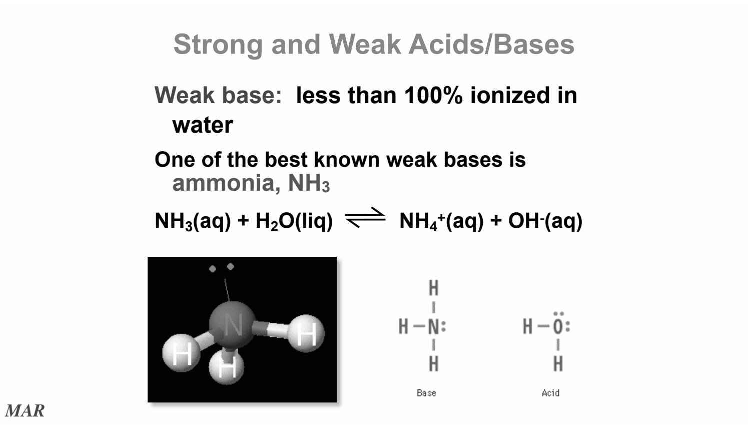
Other strong *monobasic* bases: KOH, LiOH

$Ca(OH)_2$ is a strong *dibasic* system:

CaO (lime) + H_2O --> $Ca(OH)_2$ (slaked lime)

Memorize the three strong monobasic bases!

MAR



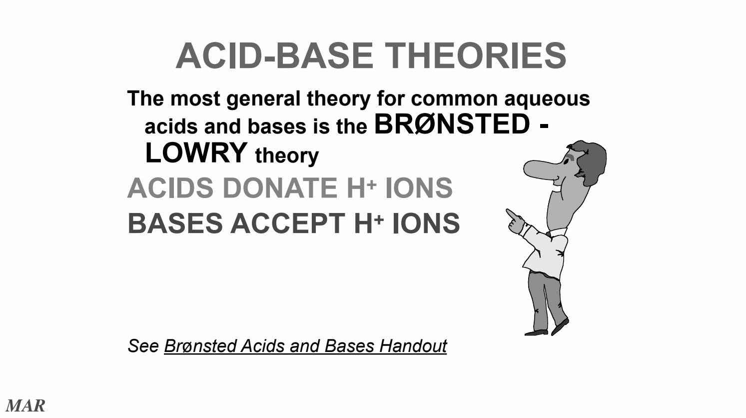
Strong and Weak Acids/Bases

Weak base: less than 100% ionized in water

One of the best known weak bases is ammonia, NH_3

$NH_3(aq) + H_2O(liq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

MAR



ACID-BASE THEORIES

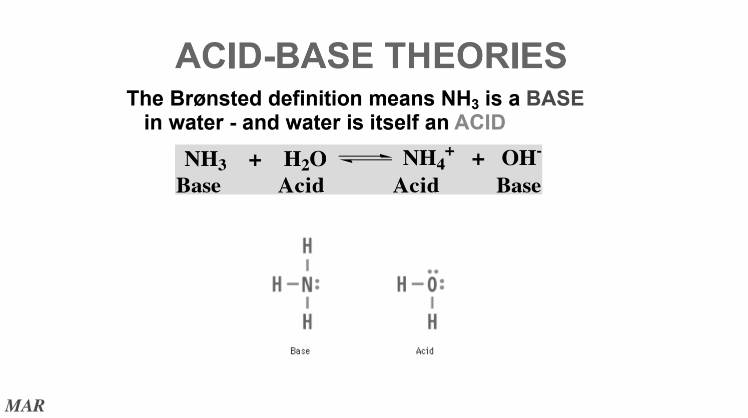
The most general theory for common aqueous acids and bases is the **BRØNSTED - LOWRY** theory

ACIDS DONATE H^+ IONS

BASES ACCEPT H^+ IONS

See *Brønsted Acids and Bases Handout*

MAR

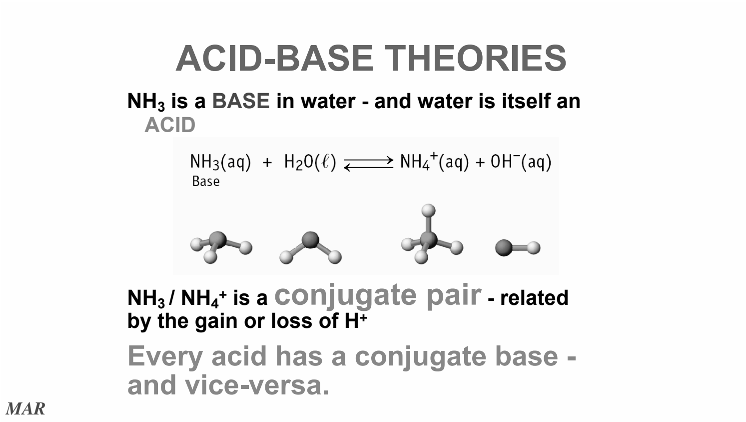


ACID-BASE THEORIES

The Brønsted definition means NH_3 is a BASE in water - and water is itself an ACID

NH_3	+	H_2O	$\rightleftharpoons$	NH_4^+	+	OH^-
Base		Acid		Acid		Base

MAR



ACID-BASE THEORIES

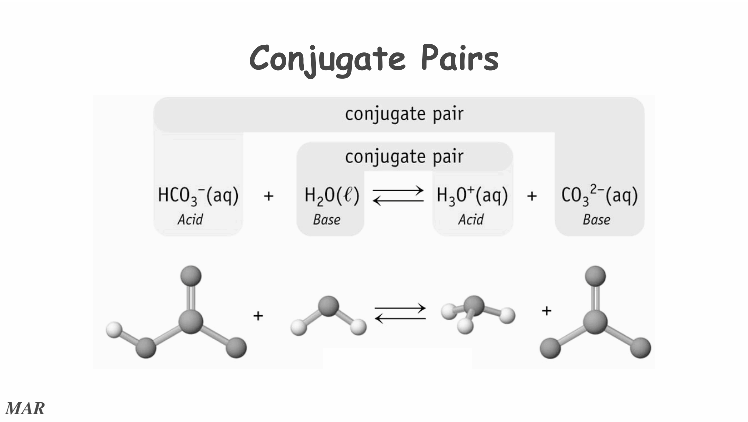
NH_3 is a BASE in water - and water is itself an ACID

$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

NH_3 / NH_4^+ is a conjugate pair - related by the gain or loss of H^+

Every acid has a conjugate base - and vice-versa.

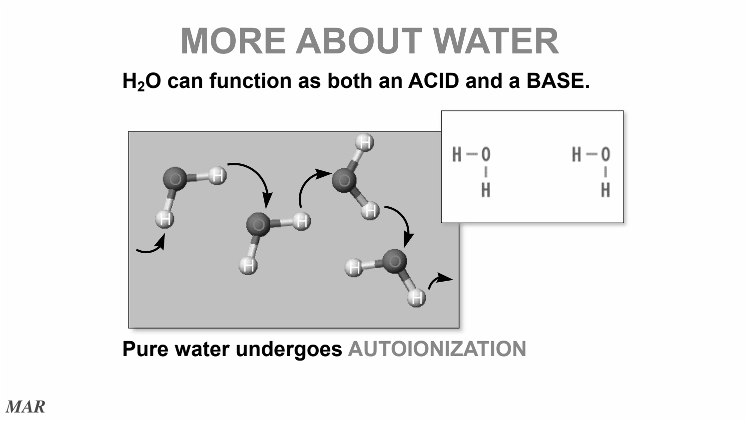
MAR



Conjugate Pairs

$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

MAR

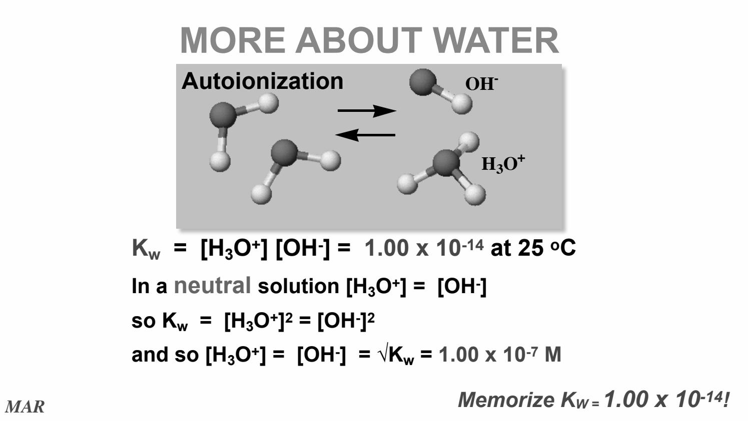


MORE ABOUT WATER

H_2O can function as both an ACID and a BASE.

Pure water undergoes AUTOIONIZATION

MAR



MORE ABOUT WATER

K_w = $[H_3O^+][OH^-]$ = 1.00×10^{-14} at 25 °C

In a neutral solution $[H_3O^+]$ = $[OH^-]$

so K_w = $[H_3O^+]^2 = [OH^-]^2$

and so $[H_3O^+]$ = $[OH^-]$ = $\sqrt{K_w}$ = 1.00×10^{-7} M

Memorize $K_W = 1.00 \times 10^{-14}$!

MAR

Calculating $[H_3O^+]$ & $[OH^-]$

You add 0.0010 mol of NaOH to 1.0 L of pure water. Calculate $[H_3O^+]$ and $[OH^-]$.

Solution

$2\ H_2O(liq) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

Le Chatelier predicts equilibrium shifts to the ____________.

$[H_3O^+] < 10^{-7}$ at equilibrium.

Set up an ICE concentration table.

MAR

Calculating $[H_3O^+]$ & $[OH^-]$

You add 0.0010 mol of NaOH to 1.0 L of pure water. Calculate $[H_3O^+]$ and $[OH^-]$.

Solution

$2\ H_2O(liq) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

initial
change
equilib

$K_w = (x)(0.0010 + x)$

Because $x << 0.0010$ M, *assume* $[OH^-] = 0.0010$ M

$K_w = (x)(0.0010 + x) \approx (x)(0.0010) = [H_3O^+](0.0010)$

$[H_3O^+] = K_w / 0.0010 = 1.0 \times 10^{-11}$ M

MAR

Calculating $[H_3O^+]$ & $[OH^-]$

You add 0.0010 mol of NaOH to 1.0 L of pure water. Calculate $[H_3O^+]$ and $[OH^-]$.

Solution

$2\ H_2O(liq) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

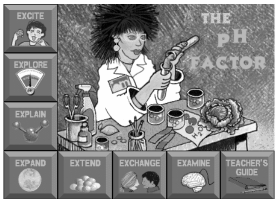
$[H_3O^+] = K_w / 0.0010 = 1.0 \times 10^{-11}$ M

$[OH^-] = 1.0 \times 10^{-3}$ M

This solution is ____________

because

$[OH^-] > [H_3O^+]$



MAR

$[H_3O^+]$, $[OH^-]$ and pH

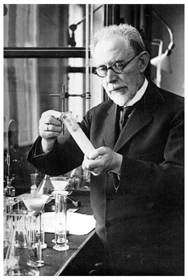
A common way to express acidity and basicity is with pH

$pH = -\log [H_3O^+]$

In a *neutral* solution,
$[H_3O^+] = [OH^-] =$
1.0×10^{-7} at 25 °C

$pH = -\log (1.00 \times 10^{-7})$
$= -(-7.00) = 7.00$

pH = 7.00 for neutral solutions!



***Søren Sørensen**, creator of the pH scale*

MAR

$[H_3O^+]$, $[OH^-]$ and pH

What is the pH of the 0.0010 M NaOH solution?

$[H_3O^+] = 1.0 \times 10^{-11}$ M

$pH = -\log (1.0 \times 10^{-11}) = 11.00$

General conclusion -

Basic solution	**pH > 7**
Neutral	**pH = 7**
Acidic solution	**pH < 7**

Public Enemy are not scientists!

MAR

$[H_3O^+]$, $[OH^-]$ and pH

If the pH of Diet Coke is 3.12, it is ____________.

Because $pH = -\log [H_3O^+]$ then

$\log [H_3O^+] = -pH$

Take antilog and get

$[H_3O^+] = 10^{-pH}$

$[H_3O^+] = 10^{-3.12}$

$= 7.6 \times 10^{-4}$ M

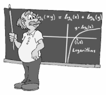
MAR

logarithms and sig figs

Logarithms are exponents with special sig figs rules. *General rule:*

log of experimentally measured number with *N* sig figs give numbers with *N* decimal places *after* the decimal (digit before decimal only indicates magnitude)

***Examples*:**



log $3.07*10^{-3}$ = -2.513 (*3 sigs, 3 places after decimal)*

- log $1.1*10^{-8}$ = 7.96 (*2 sigs, 2 places after decimal)*

$10^{-3.12}$ = 7.6 * 10^{-4} *(2 places after decimal, 2 sigs)*

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pH of Common Substances

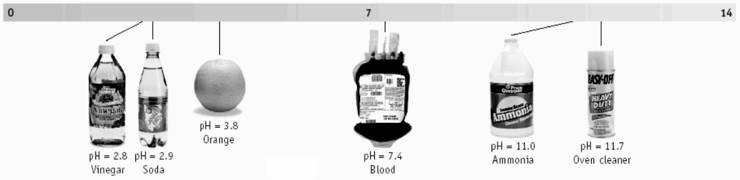


Figure 5.17 pH values of some common substances. Here the "bar" is colored red at one end and blue at the other. These are the colors of litmus paper, commonly used in the laboratory to decide if a solution is acidic (litmus is red) or basic (litmus is blue). *(Charles D. Winters)*

MAR

Other pX Scales

In general	**pX = -log X**
and:	**pK_a = - log K_a**
and so:	**pOH = - log [OH^-]**

K_w = [H_3O^+] [OH^-] = 1.00 x 10^{-14} *at 25 °C*

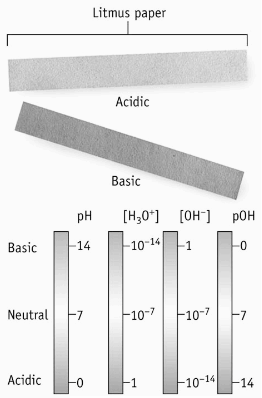
Take the negative log of both sides

-log (10^{-14}) = - log [H_3O^+] + (-log [OH^-])

14 = pH + pOH

also: **14 = pK_a + pK_b**

MAR



MAR

acidic solutions:

pH ↓,

[H_3O^+] ↑,

[OH^-] ↓,

pOH ↑

basic solutions: **pH ↑,**

[H_3O^+] ↓,

[OH^-] ↑,

pOH ↓

K_w = [H_3O^+] [OH^-] = 1.00 x 10^{-14} at 25 ˚C

pH + pOH = 14

Equilibria Considerations Involving Weak Acids and Bases

Acid	Conjugate Base
acetic, CH_3CO_2H	**$CH_3CO_2^-$, acetate**
ammonium, NH_4^+	**NH_3, ammonia**
bicarbonate, HCO_3^-	**CO_3^{2-}, carbonate**

A weak acid (or base) is one that ionizes to a VERY small extent (< 5%).

MAR

Equilibria Involving Weak Acids and Bases

Consider acetic acid, CH_3CO_2H (HOAc)

$$\underset{\text{Acid}}{\text{HOAc}} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{Conj. base}}{\text{OAc}^-}$$

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.8 \text{ x } 10^{-5}$$

(K is designated K_a for ACID)

Because [H_3O^+] and [OAc^-] are SMALL, K_a << 1.

MAR

Equilibrium Constants for Weak Acids (K_a)

$$HA(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Weak acids have $K_a < 1$
Leads to small $[H_3O^+]$ and a pH of 2 - 7

MAR

Equilibrium Constants for Weak Bases (K_b)

$$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Weak bases have $K_b < 1$
Leads to small $[OH^-]$ and a pH of 12 - 7

MAR

Equilibrium Constants for Weak Acids and Bases

$\cancel{HA} + H_2O \rightleftharpoons H_3O^+ + \cancel{A^-}$ K_a

$\cancel{A^-} + H_2O \rightleftharpoons \cancel{HA} + OH^-$ K_b

\-------------------------------------

$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$ $K_a{*}K_b = K_w$

Important relations: $K_a{*}K_b = K_w$ and $pK_a + pK_b = 14$

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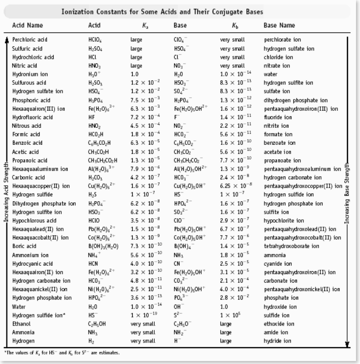
Ionization Constants for Acids/Bases

Acids

Increase strength



Ionization Constants for Some Acids and Their Conjugate Bases

Acid Name	Acid	K_a	Base	K_b	Base Name
Perchloric acid	$HClO_4$	large	ClO_4^-	very small	perchlorate ion
Sulfuric acid	H_2SO_4	large	HSO_4^-	very small	hydrogen sulfate ion
Hydrochloric acid	HCl	large	Cl^-	very small	chloride ion
Nitric acid	HNO_3	large	NO_3^-	very small	nitrate ion
Hydronium ion	H_3O^+	1.0	H_2O	1.0×10^{-14}	water
Sulfurous acid	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	sulfate ion
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	dihydrogen phosphate ion
Hexaaquairon(III) ion	$Fe(H_2O)_6^{3+}$	6.3×10^{-3}	$Fe(H_2O)_5OH^{2+}$	1.6×10^{-12}	pentaaquahydroxoiron(III) ion
Hydrofluoric acid	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	fluoride ion
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	nitrite ion
Formic acid	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	formate ion
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	benzoate ion
Acetic acid	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	acetate ion
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	propanoate ion
Hexaaqualuminum ion	$Al(H_2O)_6^{3+}$	7.9×10^{-6}	$Al(H_2O)_5OH^{2+}$	1.3×10^{-9}	pentaaquahydroxoaluminum ion
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	hydrogen carbonate ion
Hexaaquacopper(II) ion	$Cu(H_2O)_6^{2+}$	1.6×10^{-7}	$Cu(H_2O)_5OH^+$	6.25×10^{-8}	pentaaquahydroxocopper(II) ion
Hydrogen sulfide	H_2S	1×10^{-7}	HS^-	1×10^{-7}	hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}	hydrogen phosphate ion
Hydrogen sulfite ion	HSO_3^-	6.2×10^{-8}	SO_3^{2-}	1.6×10^{-7}	sulfite ion
Hypochlorous acid	$HClO$	3.5×10^{-8}	ClO^-	2.9×10^{-7}	hypochlorite ion
Hexaaqualead(II) ion	$Pb(H_2O)_6^{2+}$	1.5×10^{-8}	$Pb(H_2O)_5OH^+$	6.7×10^{-7}	pentaaquahydroxolead(II) ion
Hexaaquacobalt(II) ion	$Co(H_2O)_6^{2+}$	1.3×10^{-9}	$Co(H_2O)_5OH^+$	7.7×10^{-6}	pentaaquahydroxocobalt(II) ion
Boric acid	$B(OH)_3(H_2O)$	7.3×10^{-10}	$B(OH)_4^-$	1.4×10^{-5}	tetrahydroxoborate ion
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}	ammonia
Hydrocyanic acid	HCN	4.0×10^{-10}	CN^-	2.5×10^{-5}	cyanide ion
Hexaaquairon(II) ion	$Fe(H_2O)_6^{2+}$	3.2×10^{-10}	$Fe(H_2O)_5OH^+$	3.1×10^{-5}	pentaaquahydroxoiron(II) ion
Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}	carbonate ion
Hexaaquanickel(II) ion	$Ni(H_2O)_6^{2+}$	2.5×10^{-11}	$Ni(H_2O)_5OH^+$	4.0×10^{-4}	pentaaquahydroxonickel(II) ion
Hydrogen phosphate ion	HPO_4^{2-}	3.6×10^{-13}	PO_4^{3-}	2.8×10^{-2}	phosphate ion
Water	H_2O	1.0×10^{-14}	OH^-	1.0	hydroxide ion
Hydrogen sulfide ion*	HS^-	1×10^{-19}	S^{2-}	1×10^{5}	sulfide ion
Ethanol	C_2H_5OH	very small	$C_2H_5O^-$	large	ethoxide ion
Ammonia	NH_3	very small	NH_2^-	large	amide ion
Hydrogen	H_2	very small	H^-	large	hydride ion

*The values of K_a for HS^- and K_b for S^{2-} are estimates.

Conjugate Bases

Increase strength

MAR

K and Acid-Base Reactions

ACIDS	CONJUGATE BASES
STRONG	weak
↑	↓
weak	STRONG

In general, **Reactions always go from the** stronger A-B pair (larger K) **to the** weaker A-B pair (smaller K).

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K and Acid-Base Reactions

A strong acid is 100% dissociated.

Therefore, a STRONG ACID **- a good H^+ donor- must have a** WEAK CONJUGATE BASE **- a poor H^+ acceptor.**

$HNO_3(aq) + H_2O(liq) \rightleftharpoons H_3O^+(aq) + NO_3^-(aq)$

STRONG A base acid weak B

***Every* A-B reaction has two acids and two bases.**
Equilibrium always lies *toward the weaker pair.*
Here K is *very* large... should write:
$HNO_3(aq) + H_2O(liq) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

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K and Acid-Base Reactions

Acetic acid is only 0.42% ionized when [HOAc] = 1.0 M. It is a WEAK ACID

HOAc	**+**	**H_2O**	**$\rightleftharpoons$**	**H_3O^+**	**+**	**OAc^-**
WEAK A		**base**		**acid**		**STRONG B**

Because $[H_3O^+]$ is small, this must mean

1. **H_3O^+ is a stronger acid than HOAc**
2. **OAc^- is a stronger base than H_2O**
3. **K for this reaction is small**

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Types of Acid/Base Reactions

1. Strong acid + Strong base (SA + SB) reactions:

$HCl(aq) + NaOH(aq) \rightleftharpoons H_2O(l) + NaCl(aq)$

$H^+ + Cl^- + Na^+ + OH^- \rightleftharpoons H_2O + Na^+ + Cl^-$

Net ionic equation:

$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(liq)$

$K = 1/K_w = 1 \times 10^{14}$ ***very product favored K!***

Mixing equal molar quantities of a strong acid and strong base produces a neutral solution.

should write:

$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$

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Types of Acid/Base Reactions

2. Weak acid + Strong base (WA + SB) reactions:

$CH_3CO_2H + OH^- \rightleftharpoons H_2O + CH_3CO_2^-$

This is the reverse of the reaction of $CH_3CO_2^-$ (conjugate base) with H_2O.

OH^- stronger base than $CH_3CO_2^-$

$K = 1/K_b = 1.8 \times 10^9$ ***very product favored K!***

Mixing equal molar quantities of a weak acid and strong base produces the acid's conjugate base. The solution is basic.

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Types of Acid/Base Reactions

3. Weak base + Strong acid (WB + SA) reactions:

$H_3O^+ + NH_3 \rightleftharpoons H_2O + NH_4^+$

This is the reverse of the reaction of NH_4^+ (conjugate acid of NH_3) with H_2O.

H_3O^+ stronger acid than NH_4^+

$K = 1/K_a = 1.8 \times 10^9$ ***very product favored K!***

Mixing equal molar quantities of a strong acid and weak base produces the base's conjugate acid. The solution is acidic.

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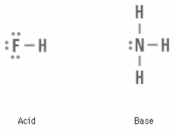
Types of Acid/Base Reactions

4. Weak acid + weak base (WA + WB) reactions:



Product cation = conjugate acid of weak base.
Product anion = conjugate base of weak acid.
pH of solution depends on relative strengths of cation and anion (larger K → smaller K).

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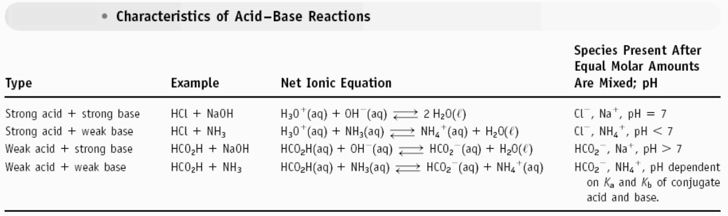
We will not be studying WA + WB reactions in CH 223

Types of Acid/Base Reactions: Summary



• Characteristics of Acid–Base Reactions

Type	Example	Net Ionic Equation	Species Present After Equal Molar Amounts Are Mixed; pH
Strong acid + strong base	HCl + NaOH	$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2\,H_2O(\ell)$	Cl^-, Na^+, pH = 7
Strong acid + weak base	$HCl + NH_3$	$H_3O^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + H_2O(\ell)$	Cl^-, NH_4^+, pH < 7
Weak acid + strong base	$HCO_2H + NaOH$	$HCO_2H(aq) + OH^-(aq) \rightleftharpoons HCO_2^-(aq) + H_2O(\ell)$	HCO_2^-, Na^+, pH > 7
Weak acid + weak base	$HCO_2H + NH_3$	$HCO_2H(aq) + NH_3(aq) \rightleftharpoons HCO_2^-(aq) + NH_4^+(aq)$	HCO_2^-, NH_4^+, pH dependent on K_a and K_b of conjugate acid and base.

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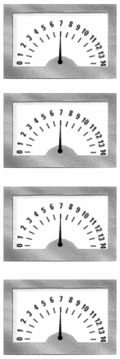

0.0001 M

0.003 M

0.06 M

2.0 M

a pH meter

Equilibria Involving A Weak Acid

Determining the pH of an acetic acid solution

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc^-, and the pH.

Step 1. **Define ICE equilibrium using K_a.**

$$\text{HOAc} + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

	[HOAc]	$[H_3O^+]$	$[OAc^-]$
initial			
change			
equilib			

Note that we neglect $[H_3O^+]$ from H_2O.

HOAc = acetic acid, OAc^- = acetate ion

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc^-, and the pH.

$$\text{HOAc} + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

Step 2. **Write K_a expression**

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{x^2}{1.00 - x}$$

This is a quadratic equation; solve using the quadratic formula.

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc^-, and the pH.

Step 3. **Solve K_a expression**

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{x^2}{1.00 - x}$$

First assume x is *very small* because K_a is so small. If so:

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{x^2}{1.00}$$

Therefore,

x = $[H_3O^+]$ = $[OAc^-]$ = $[1.8\text{x}10^{-5} \bullet 1.00]^{1/2}$ = $[K_a \bullet C_a]^{1/2}$

C_a = concentration (M) of acid

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc^-, and the pH.

Step 3. **Solve K_a *approximate* expression:**

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{x^2}{1.00}$$

x = $[H_3O^+]$ = $[OAc^-]$ = $[1.8\text{x}10^{-5} \bullet 1.00]^{1/2}$

x = $[H_3O^+]$ = $[OAc^-]$ = $4.2 \text{ x } 10^{-3}$ M

pH = - log $[H_3O^+]$ = -log ($4.2 \text{ x } 10^{-3}$) = 2.37

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Exact solution with quadratic: x = 0.0042, x = -0.0043

Equilibria Involving A Weak Acid

Consider the approximate expression:

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{x^2}{1.00} \qquad x = [H_3O^+] = [K_a \bullet 1.00]^{1/2}$$

For many weak acids

$[H_3O^+]$ = [conj. base] = $[K_a \cdot C_a]^{1/2}$

where C_a = initial conc. of acid

Useful Rule of Thumb:

If $100 \cdot K_a < C_a$, then $[H_3O^+] = [K_a \cdot C_a]^{1/2}$

or pH = - log $[K_a \cdot C_a]^{1/2}$

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Equilibria Involving A Weak Acid

Calculate the pH of a 0.0010 M solution of formic acid, HCO_2H.

$$HCO_2H + H_2O \rightleftharpoons HCO_2^- + H_3O^+$$

$K_a = 1.8 \times 10^{-4}$

100 * K_a is not less than C_a!

Approximate solution

$[H_3O^+] = [K_a \cdot C_a]^{1/2} = 4.2 \times 10^{-4}$ M, pH = 3.37

Exact Solution

$[H_3O^+] = [HCO_2^-] = 3.4 \times 10^{-4}$ M

$[HCO_2H] = 0.0010 - 3.4 \times 10^{-4} = 0.0007$ M

pH = 3.47

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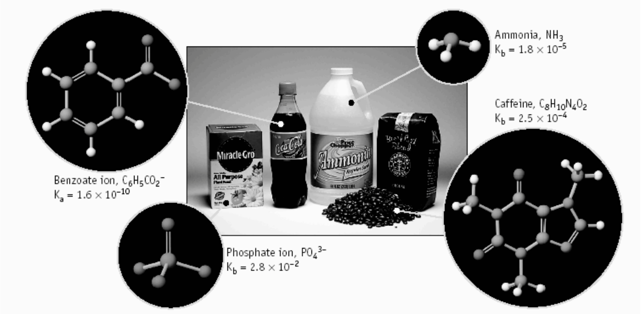
Weak Bases



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Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$K_b = 1.8 \times 10^{-5}$

Step 1. **Define equilibrium concs.**

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial			
change			
equilib			

MAR

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$K_b = 1.8 \times 10^{-5}$

Step 2. **Solve the equilibrium expression**

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.010 - x}$$

Assume **x is small ($100 \cdot K_b < C_b$)**, *so*

$x = [OH^-] = [NH_4^+] = [K_b \cdot C_b]^{1/2} = 4.2 \times 10^{-4}$ M

check: **$[NH_3] = 0.010 - 4.2 \times 10^{-4} \approx 0.010$ M**

Valid approximation!

Exact solution with quadratic: x = 0.00042, x = -0.00043

MAR

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$K_b = 1.8 \times 10^{-5}$

Step 3. **Calculate pH**

$[OH^-] = 4.2 \times 10^{-4}$ M

so pOH = - log $[OH^-]$ = 3.37

Because pH + pOH = 14,

pH = 10.63

***or* pH = 14 + log $[K_b \cdot C_b]^{1/2}$ = 10.63**

MAR

Overview: Calculating pH of Acids & Bases

Strong acid: **pH = - log C_a = - log $[H_3O^+]$**

Strong base:

pH = 14 + log C_b = 14 + log $[OH^{-1}]$

Weak acid:

pH = - log $[K_a \cdot C_a]^{1/2}$ *($100 * K_a < C_a$)*

Weak base:

pH = 14 + log $[K_b \cdot C_b]^{1/2}$ *($100 * K_b < C_b$)*

Memorize!

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Acid-Base Properties of Salts

MX + H_2O ----> acidic or basic solution?

Consider NH_4Cl

NH_4Cl(aq) ----> NH_4^+(aq) + Cl^-(aq)

(a) Reaction of Cl^- with H_2O

Cl^-	+	H_2O	---->	HCl	+	OH^-
base		acid		acid		base

Cl^- ion is a VERY weak base because its conjugate acid is strong.

Therefore, Cl^- ----> neutral solution

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Acid-Base Properties of Salts

MX + H_2O ----> acidic or basic solution?

NH_4Cl(aq) ----> NH_4^+(aq) + Cl^-(aq)

(b) Reaction of NH_4^+ with H_2O

NH_4^+	+	H_2O	---->	NH_3	+	H_3O^+
acid		base		base		acid

NH_4^+ ion is a moderate acid ($K_a = 5.6 \times 10^{-10}$) because its conjugate base is weak.

Therefore, NH_4^+ ----> acidic solution

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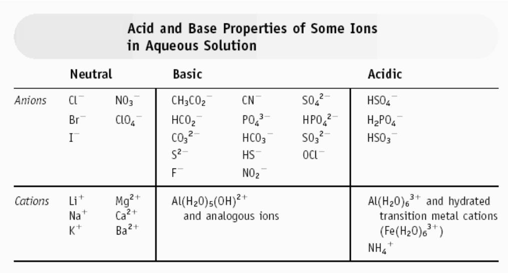
Acid-Base Properties of Salts



Acid and Base Properties of Some Ions in Aqueous Solution

	Neutral		Basic			Acidic
Anions	Cl^- Br^- I^-	NO_3^- ClO_4^-	$CH_3CO_2^-$ HCO_2^- CO_3^{2-} S^{2-} F^-	CN^- PO_4^{3-} HCO_3^- HS^- NO_2^-	SO_4^{2-} HPO_4^{2-} SO_3^{2-} OCl^-	HSO_4^- $H_2PO_4^-$ HSO_3^-
Cations	Li^+ Na^+ K^+	Mg^{2+} Ca^{2+} Ba^{2+}	$Al(H_2O)_5(OH)^{2+}$ and analogous ions			$Al(H_2O)_6^{3+}$ and hydrated transition metal cations ($Fe(H_2O)_6^{3+}$) NH_4^+

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Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na_2CO_3.

Na^+ + H_2O ---> neutral

CO_3^{2-} +	H_2O $\rightleftharpoons$	HCO_3^-	+	OH^-
base	acid	acid		base

$K_b = 2.1 \times 10^{-4}$

Step 1. Set up ICE concentration table

	$[CO_3^{2-}]$	$[HCO_3^-]$	$[OH^-]$
initial			
change			
equilib			

MAR

Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na_2CO_3.

Na^+ + H_2O ---> neutral

CO_3^{2-} +	H_2O $\rightleftharpoons$	HCO_3^-	+	OH^-
base	acid	acid		base

$K_b = 2.1 \times 10^{-4}$

Step 2. Solve the equilibrium expression

$$K_b = 2.1 \times 10^{-4} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{x^2}{0.10 - x}$$

Assume **0.10 - x ≈ 0.10,** *because* **$100 \cdot K_b < C_b$**

x = $[HCO_3^-]$ = $[OH^-]$ = $[K_b \cdot C_b]^{1/2}$ = 0.0046 M

MAR

Exact solution with quadratic: x = 0.0045, x = -0.0047

Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na_2CO_3.

Na^+ + H_2O ---> neutral

CO_3^{2-} +	H_2O $\rightleftharpoons$	HCO_3^-	+	OH^-
base	acid	acid		base

$K_b = 2.1 \times 10^{-4}$

Step 3. Calculate the pH

$[OH^-]$ = 0.0046 M

pOH = - log $[OH^-]$ = 2.34

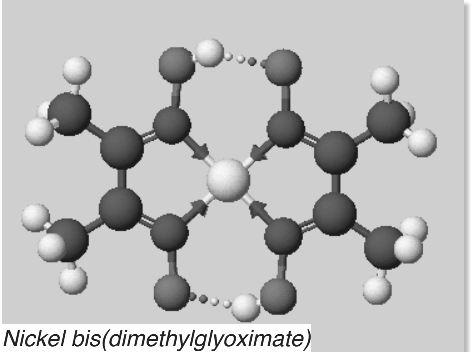
pH + pOH = 14,

so pH = 11.66, and the solution is ________.

***or* pH = 14 + log $[K_b \cdot C_b]^{1/2}$ = 11.66**

MAR

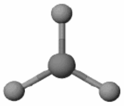
Lewis Acids & Bases


Nickel bis(dimethylglyoximate)


Clifford and Aiden with red Nickel bis(dimethylglyoximate) solution (April 2023)

Lewis Acids & Bases

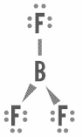
Lewis acid = electron pair acceptor (BF_3)


BF_3, the boron atom is surrounded by only three electron pairs.

Lewis base = electron pair donor (NH_3)

MAR

Lewis Acids & Bases



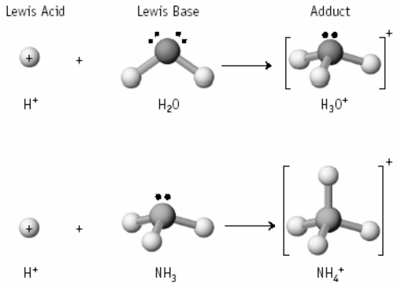
New bond formed using electron pair from the Lewis base.

Coordinate covalent bond

Notice geometry change on reaction.

MAR

Lewis Acids & Bases



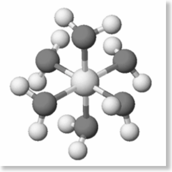
MAR

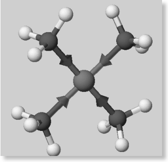
Lewis Acids & Bases

The combination of metal ions (Lewis acids) with Lewis bases such as H_2O and NH_3 ------>

COMPLEX IONS

***All* metal ions form complex ions with water and are of the type $[M(H_2O)_x]^{n+}$ where x = 4 and 6.**

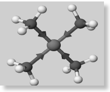

$[Co(H_2O)_6]^{3+}$

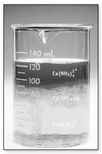

$[Cu(NH_3)_4]^{2+}$

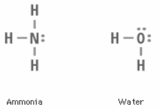
MAR

Lewis Acids & Bases

Add NH_3 to light blue $[Cu(H_2O)_4]^{2+}$ ------> light blue $Cu(OH)_2$ and then deep blue $[Cu(NH_3)_4]^{2+}$







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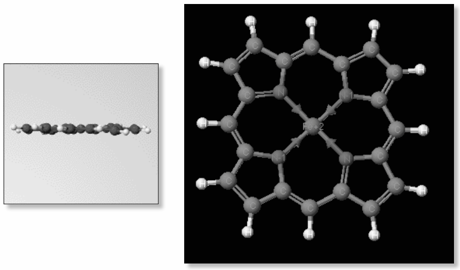
Lewis Acids & Bases

The Fe^{2+} in heme can interact with O_2 or CO in a Lewis acid-base reaction.



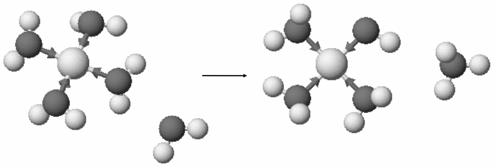
MAR

Lewis Acids & Bases

Many complex ions containing water undergo HYDROLYSIS to give acidic solutions.

$[Cu(H_2O)_4]^{2+} + H_2O \text{ ---> } [Cu(H_2O)_3(OH)]^+ + H_3O^+$

This is a K_a expression



This explains why water solutions of transition metals are acidic.

MAR

Lewis Acids & Bases

Lewis acid & base theory explains AMPHOTERIC nature of some metal hydroxides.

$Al(OH)_3(s) + 3 H^+ \text{ --> } Al^{3+} + 3 H_2O$

Here $Al(OH)_3$ is a Brønsted base.

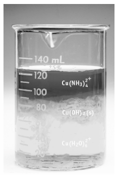
$Al(OH)_3(s) + OH^- \text{ --> } Al(OH)_4^-$

Here $Al(OH)_3$ is a Lewis acid.

$Al^{3+} \leftarrow :\ddot{\underset{..}{O}}-H^-$

MAR

Lewis Acids & Bases



Many complex ions are very stable.

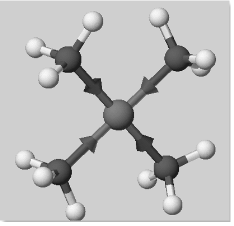
$Cu^{2+} + 4 NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$

K for the reaction is called $K_{formation}$

or a "formation constant"

Here $K_f = 6.8 \times 10^{12}$. Reaction is strongly product-favored.

$$K_f = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

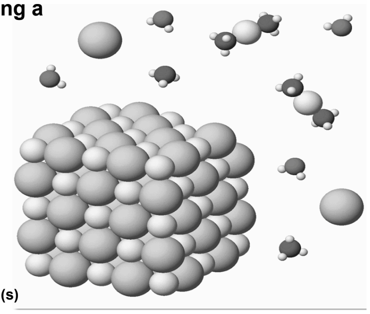


MAR

Lewis Acids & Bases

Formation of complex ions explains why you can dissolve a precipitate by forming a complex ion.

$AgCl(s) + 2 NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$



MAR

Lewis Acids & Bases

Formation of complex ions explains why you can dissolve a precipitate by forming a complex ion.

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$ $K_{sp} = 1.8 \times 10^{-10}$

$Ag^+ + 2 NH_3 \rightleftharpoons Ag(NH_3)_2^+$ $K_{form} = 1.6 \times 10^7$

$AgCl(s) + 2 NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$

$K_{net} = K_{sp} \bullet K_{form} = 2.9 \times 10^{-3}$

MAR

Hints for This Chapter

$pH_{(strong\ acid)} = - \log C_a$

$pH_{(strong\ base)} = 14 + \log C_b$

$pH_{(weak\ acid)} = - \log [K_a * C_a]^{1/2}$

$pH_{(weak\ base)} = 14 + \log [K_b * C_b]^{1/2}$

$14 = pH + pOH = pK_a + pK_b$

$K_w = 1.00 * 10^{-14} = [H_3O^+][OH^-] = K_a * K_b$ (25 °C)

***Know* equivalence point pH values for different titrations**

***Know* how to use formation constants**

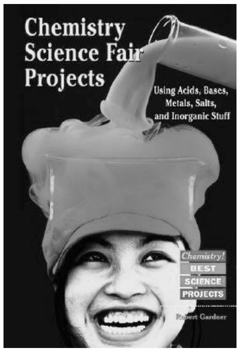
***Understand* Lewis acid/base theory**

MAR

End of Chapter 14 Part I

See:

- *Chapter Fourteen Part I Study Guide*
- *Chapter Fourteen Part I Concept Guide*
- *Types of Equilibrium Constants*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*



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Important Equations, Constants, and Handouts from this Chapter:

$pH_{(strong\ acid)} = - \log C_a$

$pH_{(strong\ base)} = 14 + \log C_b$

$pH_{(weak\ acid)} = - \log [K_a * C_a]^{1/2}$

$pH_{(weak\ base)} = 14 + \log [K_b * C_b]^{1/2}$

$14 = pH + pOH = pK_a + pK_b$

$K_w = 1.00 * 10^{-14} = [H_3O^+][OH^-] = K_a * K_b$ (25 °C)

$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]}:$$

$$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Acid-Base Theory: **Brønsted theory, conjugate acid** *and* **base, strong** *and* **weak acids** *and* **bases,** *know the* **8 strong acids** *and* **bases!, autoionization, Lewis theory, electron pair acceptor** *and* **donator, salt acidity/basicity, formation constants (K_f)**

Handouts:

- *Manipulating Equilibrium Constant Expressions*
- *Types of Equilibrium Constants*
- *Table of K_a and K_b values in Problem Set #2*

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End of Chapter Problems: *Test Yourself*

1. An aqueous solution has a pH of 3.75. What is the hydronium ion concentration of the solution? What is the hydroxide ion concentration of the solution? Is it acidic or basic?
2. What is the pH of a 0.0015 M solution of $Ba(OH)_2$?
3. Epinephrine hydrochloride has a pK_a value of 9.53. What is the value of K_a?
4. A weak base has $K_b = 4.7 \times 10^{-11}$. What is the value of K_a for the conjugate acid?
5. A 0.015 M solution of hydrogen cyanate, HOCN, has a pH of 2.67. What is the hydronium ion concentration in the solution? What is the ionization constant, K_a, for the acid?
6. A 0.015 M solution of a base has a pH of 10.09. What are the hydronium and hydroxide ion concentrations of this solution? What is the value of K_b for this base?
7. Which of the following substances should be classified as a Lewis acid and a Lewis base: $Fe^{2+}(aq)$, CH_3NH_2

MAR

End of Chapter Problems: *Answers*

1. $[H_3O^+] = 1.8 \times 10^{-4}$ M, $[OH^-] = 5.6 \times 10^{-11}$ M, acidic
2. 11.48
3. 3.0×10^{-10}
4. 2.1×10^{-4}
5. 0.0021 M, 3.6×10^{-4} ($K_a = 3.0 \times 10^{-4}$ using short method)
6. $[H_3O^+] = 8.1 \times 10^{-11}$ M, $[OH^-] = 1.2 \times 10^{-4}$ M, $K_b = 9.7 \times 10^{-7}$
7. $Fe^{2+}(aq)$ would be a Lewis acid, CH_3NH_2 would be a Lewis base

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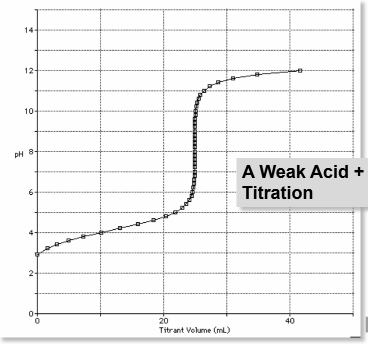
ACID-BASE REACTIONS

Chapter 14
("Part II")



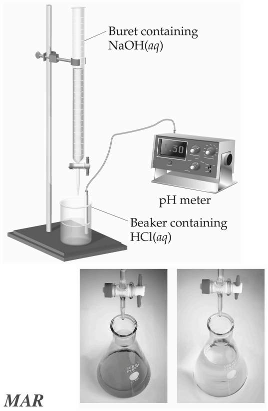
A Weak Acid + Strong Base Titration

Last update: 4/29/24

Chemistry 223
Professor Michael Russell

MAR

Titrations



In a **titration** a known concentration of base *(or acid)* is slowly added to a solution of acid *(or base)*

A **pH meter** or **indicators** are used to determine when the solution has reached the **equivalence point** (where moles of acid = moles of base)

Goal: to determine experimentally or calculate the pH at *any* point in a titration

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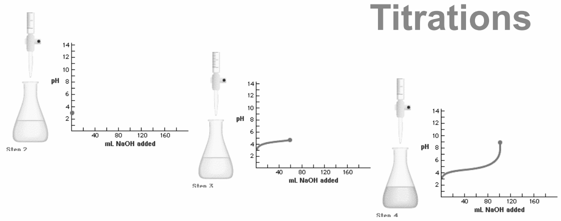
Titrations



Adding NaOH from the buret to acetic acid:

Initially the pH increases very slowly, then rises dramatically at equivalence point

pH rises, then levels off as equivalence point passed

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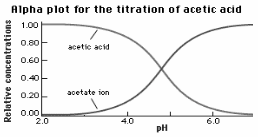
Acid-Base Titrations



Notice how [HOAc] diminishes with NaOH, *but* $[OAc^-]$ increases with NaOH

Important to consider *conjugates* in titrations where weak acids or bases dominate

But first, *buffers* and the *common ion effect*

MAR

The Common Ion Effect

A special form of Le Chatelier's Principle...

QUESTION: What is the effect on the pH of adding NH_4Cl to 0.25 M $NH_3(aq)$?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Here we are adding an ion COMMON to the equilibrium with NH_3 (*i.e.* NH_4^+)

Le Chatelier predicts that the equilibrium will shift to the ____________.

The pH will go _____________.

After all, NH_4^+ is an acid!

MAR

The Common Ion Effect

A special form of Le Chatelier's Principle...

QUESTION: What is the effect on the pH of adding NH_4Cl to 0.25 M $NH_3(aq)$?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Let us first calculate the pH of a 0.25 M NH_3 solution.

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial			
change			
equilib			

MAR

The Common Ion Effect

A special form of Le Chatelier's Principle...

QUESTION: **What is the effect on the pH of adding NH_4Cl to 0.25 M $NH_3(aq)$?**

$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = 1.8 \text{ x } 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.25 - x}$$

Assuming x is << 0.25, we have

$[OH^-] = x = [K_b(0.25)]^{1/2} = 0.0021$ M

This gives pOH = 2.67

and so pH = 14.00 - 2.67 = 11.33

or: $pH = 14 + \log [K_b \cdot C_b]^{1/2} = 11.33$

MAR

The Common Ion Effect

A special form of Le Chatelier's Principle...

Problem: **What is the pH of a solution with 0.10 M NH_4Cl *and* 0.25 M $NH_3(aq)$?**

$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

We expect that the pH will decline on adding NH_4Cl. Let's test that!

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial			
change			
equilib			

MAR

The Common Ion Effect

A special form of Le Chatelier's Principle...

Problem: **What is the pH of a solution with 0.10 M NH_4Cl *and* 0.25 M $NH_3(aq)$?**

$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = 1.8 \text{ x } 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x(0.10 + x)}{0.25 - x}$$

Because equilibrium shifts left, x is MUCH less than 0.0021 M, the value *without* NH_4Cl.

MAR

The Common Ion Effect

A special form of Le Chatelier's Principle...

Problem: **What is the pH of a solution with 0.10 M NH_4Cl *and* 0.25 M $NH_3(aq)$?**

$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = 1.8 \text{ x } 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x(0.10 + x)}{0.25 - x}$$

$[OH^-] = x = (0.25 / 0.10)K_b = 4.5 \text{ x } 10^{-5}$ M

This gives pOH = 4.35 and pH = 9.65

pH drops from 11.33 to 9.65 on adding a common ion (NH_4^+).

MAR

Buffer Solutions

The function of a buffer is to resist changes in the pH of a solution.

Buffers invoke a special case of the common ion effect.

Buffer Composition:

<u>Weak Acid</u>	+	<u>Conj. Base</u>
HOAc	+	OAc^-
$H_2PO_4^-$	+	HPO_4^{2-}
<u>Weak Base</u>	+	<u>Conj. Acid</u>
NH_3	+	NH_4^+

MAR

<u>Buffers and Henderson-Hasselbalch Guide</u>

Buffer Solutions

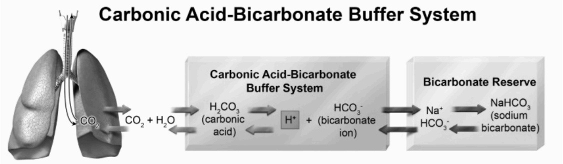
HCl is added to pure water.

HCl is added to a solution of a weak acid $H_2PO_4^-$ and its conjugate base HPO_4^{2-}.

MAR

Buffers in Our Bodies

The blood pH in our bodies is regulated by a carbonic acid / hydrogen carbonate ("bicarbonate") buffer system:



$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^{-1}$

Exhaling CO_2 raises the pH of our blood!

Buffer Solutions

Consider HOAc/OAc^- to see how buffers work

The weak acid in buffers consumes strong base!

We know:

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$$

$$K_b = 5.6 \times 10^{-10}$$

Therefore, the *reverse* reaction of the *weak acid* with added OH^- (strong base) would be:

$$HOAc + OH^- \rightleftharpoons OAc^- + H_2O$$

and: $K_{reverse} = 1/K_b = 1.8 \times 10^9$

$K_{reverse}$ is VERY large, so HOAc completely consumes the OH^-!

Buffer Solutions

Consider HOAc/OAc^- to see how buffers work

Conjugate base in buffers consumes strong acid!

$$HOAc + H_2O \rightleftharpoons OAc^- + H_3O^+$$

$$K_a = 1.8 \times 10^{-5}$$

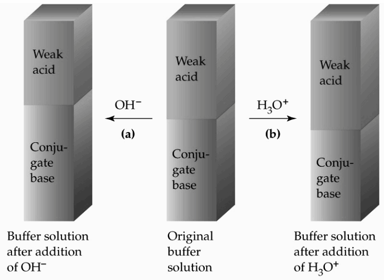
Therefore, the *reverse* reaction of the weak base with added H_3O^+ (strong acid) would be:

$$OAc^- + H_3O^+ \rightleftharpoons HOAc + H_2O$$

$$K_{reverse} = 1/K_a = 5.6 \times 10^4$$

$K_{reverse}$ is VERY LARGE, so OAc^- completely consumes the H_3O^+!

Buffer Solutions



Buffer Solutions

Problem: What is the pH of a buffer that has [HOAc] = 0.700 M and [OAc^-] = 0.600 M?

$HOAc + H_2O \rightleftharpoons OAc^- + H_3O^+$

$K_a = 1.8 \times 10^{-5}$

	[HOAc]	[OAc^-]	[H_3O^+]
initial			
change			
equilib			

Buffer Solutions

Problem: What is the pH of a buffer that has [HOAc] = 0.700 M and [OAc^-] = 0.600 M?

$HOAc + H_2O \rightleftharpoons OAc^- + H_3O^+$

$K_a = 1.8 \times 10^{-5}$

	[HOAc]	[OAc^-]	[H_3O^+]
equilib	0.700 - x	0.600 + x	x

Assuming that x << 0.700 and 0.600, we have

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+](0.600)}{0.700}$$

$[H_3O^+] = 1.8 \times 10^{-5} * (0.700 / 0.600) = 2.1 \times 10^{-5}$ *and*

pH = 4.68

Buffer Solutions

Notice that the expression for calculating the H^+ conc. of the buffer is:

$$[H_3O^+] = \frac{\text{Orig. conc. of HOAc}}{\text{Orig. conc. of OAc}^-} \bullet K_a$$

$$[H_3O^+] = \frac{[\text{Acid}]}{[\text{Conj. base}]} \bullet K_a \quad \textit{or} \quad [OH^-] = \frac{[\text{Base}]}{[\text{Conj. acid}]} \bullet K_b$$

Notice that $[H_3O^+]$ or $[OH^-]$ depend on K and the ratio of acid and base concentrations

MAR

Henderson-Hasselbalch Equation

$$[H_3O^+] = \frac{[\text{Acid}]}{[\text{Conj. base}]} \bullet K_a$$

Take the negative log of both sides of this equation:

$$pH = pK_a - \log\frac{[\text{Acid}]}{[\text{Conj. base}]}$$

The Henderson - Hasselbalch Eq!

$$pH = pK_a + \log\frac{[\text{Conj. base}]}{[\text{Acid}]}$$

The pH is determined largely by the pK_a of the acid and then adjusted by the ratio of acid and conjugate base. *Important equation!*

MAR

Henderson-Hasselbalch Equation

$$pH = pK_a + \log\frac{[\text{Conj. base}]}{[\text{Acid}]}$$

Note that the CONCENTRATIONS of the acid and conjugate base are not important.

It is the RATIO of the NUMBER OF MOLES that affects pH

Result: **diluting a buffer solution does not change its pH**

Result: **You can use moles or molarity when using Henderson-Hasselbalch!**

See: *Buffers and Henderson-Hasselbalch Guide*

MAR

Adding an Acid to a Buffer

Problem: What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water (before HCl, pH = 7.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc-] = 0.600 M (pH = 4.68)

Solution to Part (a)

pH of strong acid **= - log $[H_3O^+]$ = - log [HCl]**

$$M_1 \bullet V_1 = M_2 \bullet V_2$$

$$1.00\ M * 1.00\ mL = M_2 \bullet 1001\ mL$$

$$M_2 = 9.99 \times 10^{-4}\ M = [H_3O^+]$$

pH = 3.00

MAR

Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water (after HCl, pH = 3.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc-] = 0.600 M (pH = 4.68)

Solution to Part (b)

Step 1 - do the stoichiometry

H_3O^+ (from HCl) + OAc^- (from buffer) ---> HOAc (from buffer)

The reaction occurs completely because K is very large.

MAR

Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water (after HCl, pH = 3.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc-] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 1-Stoichiometry

	$[H_3O^+]$	$[OAc^-]$	[HOAc]
Initial			
Change			
After rxn			

Now we need to calculate pH using our new buffer solution

MAR

Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water (after HCl, pH = 3.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc-] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium

HOAc + $H_2O \rightleftharpoons H_3O^+$ + OAc^-

	[HOAc]	[OAc⁻]	[H_3O^+]
Initial			
Change			
Equilibrium			

MAR

Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water (after HCl, pH = 3.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc-] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium

HOAc + $H_2O \rightleftharpoons H_3O^+$ + OAc^-

	[HOAc]	[OAc⁻]	[H_3O^+]
Equilibrium	0.701-x	0.599+x	x

Because [H_3O^+] = 2.1 x 10^{-5} M *BEFORE* adding HCl, we again neglect x relative to 0.701 and 0.599.

MAR

Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water (after HCl, pH = 3.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc-] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium

HOAc + $H_2O \rightleftharpoons H_3O^+$ + OAc^-

$$[\mathrm{H_3O^+}] = \frac{[\mathrm{HOAc}]}{[\mathrm{OAc^-}]} \bullet K_a = \frac{0.701}{0.599} \bullet (1.8 \text{ x } 10^{-5})$$

[H_3O^+] = 2.1 x 10^{-5} M ------> pH = 4.68

The pH has not changed on adding HCl to the buffer!

MAR

Adding an Acid to a Buffer

Use the Henderson-Hasselbalch equation to calculate the pH when 1.00 mL of 1.00 M HCl is added to 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc-] = 0.600 M

We can use an *alternate* form of the H-H equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{(\mathrm{mol_{Conj\ base}} - \mathrm{mol_{strong\ acid}})}{(\mathrm{mol_{weak\ acid}} + \mathrm{mol_{strong\ acid}})}$$

$\mathrm{p}K_a = -\log(1.80 * 10^{-5}) = 4.74$

$$\mathrm{pH} = 4.74 + \log \frac{(0.600 - 0.00100)}{(0.700 + 0.00100)} = 4.67$$

Answer in good agreement with “double ice" method (4.68)

See: Buffers and Henderson-Hasselbalch Guide

MAR

Adding Acids and Bases to Buffers

For adding strong acids to buffers:

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{(\mathrm{mol_{Conj\ base}} - \mathrm{mol_{strong\ acid}})}{(\mathrm{mol_{weak\ acid}} + \mathrm{mol_{strong\ acid}})}$$

For adding strong bases to buffers:

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{(\mathrm{mol_{Conj\ base}} + \mathrm{mol_{strong\ base}})}{(\mathrm{mol_{weak\ acid}} - \mathrm{mol_{strong\ base}})}$$

*Very useful **for calculating pH changes in buffers!***

See: Buffers and Henderson-Hasselbalch Guide

MAR

Preparing a Buffer

Henderson

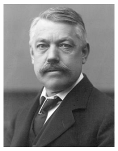
You want to create a buffer solution with a pH = 4.30.

This means [H_3O^+] = 10^{-pH} = 5.0 x 10^{-5} M

It is best to choose an acid such that:

- [H_3O^+] ≈ K_a, ***or***
- pH ≈ $\mathrm{p}K_a$

Hasselbalch



You get the *exact* [H_3O^+] (or pH) by adjusting the *ratio* of weak acid to conjugate base.

For a pH = 4.30 buffer, we will look for a value of K_a ≈ 5.0 x 10^{-5} or a $\mathrm{p}K_a$ ≈ 4.30

MAR

Preparing a Buffer

You wish to create a buffer solution at pH = 4.30 (*or* $[H_3O^+]$ = 5.0 x 10^{-5} M.) Which of these buffer combinations should you select?

POSSIBLE BUFFERS	K_a	pK_a
HSO_4^- / SO_4^{2-}	**1.2 x 10^{-2}**	**1.92**
HOAc / OAc^-	**1.8 x 10^{-5}**	**4.74**
HCN / CN^-	**4.0 x 10^{-10}**	**9.40**

Best choice is acetic acid / acetate - closest in $[H_3O^+]$ to K_a *or* pH to pK_a!

MAR

Preparing a Buffer

You want to create a buffer solution at pH = 4.30 *(or $[H_3O^+]$ = 5.0 x 10^{-5} M)* **using HOAc and OAc^{-1}.**

Equal moles of acid (HOAc) and base (OAc^{-1}) create pH = 4.74 (= pK_a). Find the ratio of acid to base needed to get the buffer to 4.30.

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]}, \textit{ or rearranged:}$$

$$[H_3O^+] = 5.0 \times 10^{-5} = \frac{[HOAc]}{[OAc^-]}\,(1.8 \times 10^{-5})$$

Solve for [HOAc] / $[OAc^-]$ ratio:

= $[H_3O^+]$ / K_a = 2.8 / 1

MAR

Preparing a Buffer

You want to create a buffer solution at pH = 4.30 (or $[H_3O^+]$ = 5.0 x 10^{-5} M). Find the ratio of acid to base needed to get the buffer to 4.30.

[HOAc] / $[OAc^-]$ **ratio = 2.8 / 1** *(previous slide)*

Therefore, if you use **0.10 mol** of NaOAc and **0.28 mol** of HOAc**, you will have pH = 4.30.**

Could have also used Henderson Hasselbalch:

$$pH = pK_a + \log\frac{[\text{Conj. base}]}{[\text{Acid}]}$$

$$4.30 = 4.74 + \log\frac{[\text{Conj. base}]}{[\text{Acid}]}$$

$$10^{-0.44} = 0.36 * {[base]}\big/{[acid]}, \textit{ invert:}$$

$$[acid]\big/[base] = 2.8$$

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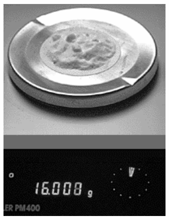
Preparing a Buffer Solution



Buffer prepared from

8.4 g $NaHCO_3$

weak acid

16.0 g Na_2CO_3

conjugate base

$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

What is the pH?

Check yourself! Answer: 10.50

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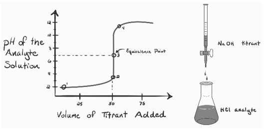
Titration Calculations

Allow us to calculate pH at any point in a titration

We will study four types of titrations:

- **SA + SB (equivalence pH = 7)**
- **SB + SA (equivalence pH = 7)**
- **WA + SB (equivalence pH > 7)**
- **WB + SA (equivalence pH < 7)**



Titrations separated into *regions* each with their own pH formula

Buffers used in WA + SB and WB + SA

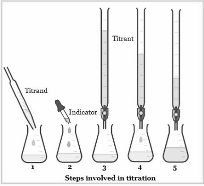
We will do examples of all four as practice in lab.

See Titration Guide

MAR

Titration Calculation Hints

- **Strong acids** and **strong bases** ***annihilate*** their opposites
- Weak acids and bases produce their ***conjugates***
- **K_a** and **K_b** may be determined through titrations or half-equivalence pH values
- *Remember:* K_a*K_b = K_w **= 1.00*10^{-14} (25 ˚C)**
- Often helpful to **find pK_a** or **pK_b**
- *Remember:* $pK_a + pK_b = 14$
- Need to know **initial concentration and volume** of titrant



Steps involved in titration

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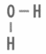
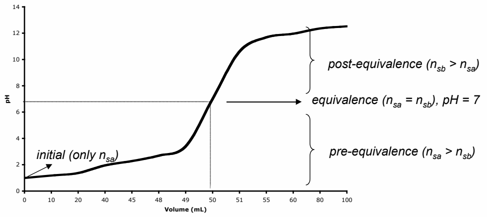
Strong Acid + Strong Base



A strong acid + strong base titration



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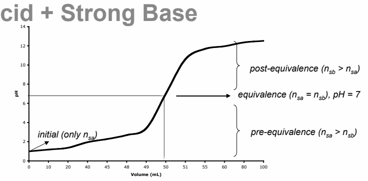
Strong Acid + Strong Base



Initial: $\mathrm{pH} = -\log [n_{sa} / V_{sa}]$

Pre-equivalence: $\mathrm{pH} = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

Equivalence: pH = 7 (neutral salt + water)

Post-equivalence: $\mathrm{pH} = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$

MAR

Acid-Base Reactions

QUESTION: **You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH of the** initial **solution?**

$HCl + H_2O \longrightarrow Cl^- + H_3O^+$

SOLUTION:

HCl is a strong acid

NaOH is a strong base

Hence, this is a strong acid + strong base titration

***Other common strong acids:* HNO_3, HBr, HI, $HClO_4$**

***Other common strong bases:* KOH, LiOH**

MAR

Acid-Base Reactions

QUESTION: **You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH of the** initial **solution?**

$HCl + H_2O \longrightarrow Cl^- + H_3O^+$

SOLUTION:

For strong acids, $\mathrm{pH} = -\log[H_3O^+]$

$\mathrm{pH} = -\log(0.100)$

pH = 1.000

MAR

Acid-Base Reactions

QUESTION: **You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the** pH after 45 mL of NaOH **have been added?**

$HCl + H_2O \longrightarrow Cl^- + H_3O^+$

SOLUTION:

First, determine which region **of a** strong acid **and** strong base titration **to use by *comparing mol HCl to mol NaOH***

n_{sa} **= 0.050 L * 0.100 M =** 0.0050 mol **HCl**

n_{sb} **= 0.045 L * 0.100 M =** 0.0045 mol **NaOH**

Since $n_{sa} > n_{sb}$, this pH will fall in the pre-equivalence region

MAR

Acid-Base Reactions

QUESTION: **You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the** pH after 45 mL of NaOH **have been added?**

$HCl + H_2O \longrightarrow Cl^- + H_3O^+$

From before: n_{sa} **= 0.0050 mol,** n_{sb} **= 0.0045 mol**

$$\mathrm{pH} = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$$

$$\mathrm{pH} = -\log\left(\frac{0.0050 - 0.0045}{0.050 + 0.045}\right)$$

pH = 2.3

MAR

Acid-Base Reactions

QUESTION: **You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH at the equivalence point?**

At equivalence, **HCl + NaOH ---> Na^+ + Cl^- + H_2O**

Only species present at equivalence are Na^+, Cl^- and water.

Na^+ and Cl^- are conjugates of strong bases and acids; hence, they have *no effect on the pH*

pH at equivalence point will be equal to 7 (neutral) due to presence of water

The volume required to get to equivalence:

0.0050 mol HCl * (mol NaOH / mol HCl) * (L/0.100 mol NaOH) = 0.050 L *or* 50. mL

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Acid-Base Reactions

QUESTION: **You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH after 55 mL of NaOH have been added?**

SOLUTION: *(from before, n_{sa} = 0.0050 mol)*

It took 50. mL of NaOH to reach equivalence; hence, we are now in the post-equivalence region

n_{sb} = 0.100 M * 0.055 L = 0.0055 mol

$$\mathrm{pH} = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$$

$$\mathrm{pH} = 14 + \log\left(\frac{0.0055 - 0.0050}{0.055 + 0.050}\right)$$

pH = 14 + (-2.3) = 11.7

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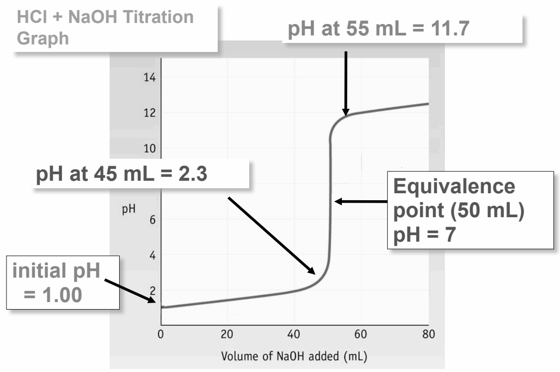
HCl + NaOH Titration Graph



pH at 55 mL = 11.7

pH at 45 mL = 2.3

Equivalence point (50 mL) pH = 7

initial pH = 1.00

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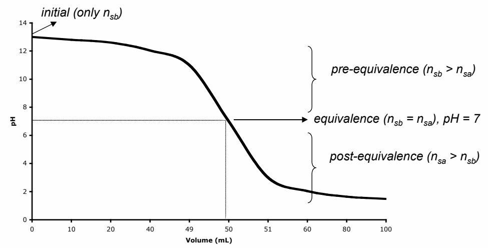
Strong Base + Strong Acid

Notice similarities between SA + SB and SB + SA titrations!

A strong base + strong acid titration



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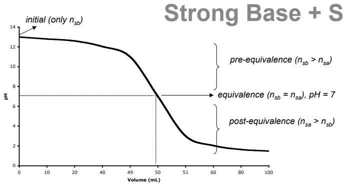
Strong Base + Strong Acid



Initial: pH = 14 + log [n_{sb} / V_{sb}]

Pre-equivalence: $\mathrm{pH} = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$

Equivalence: pH = 7 (neutral salt + water)

Post-equivalence: $\mathrm{pH} = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

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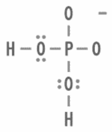
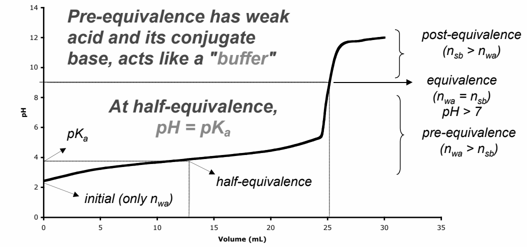
Weak Acid + Strong Base

Equivalence point dominated by conjugate base of weak acid



A weak acid + strong base titration



Pre-equivalence has weak acid and its conjugate base, acts like a "buffer"

At half-equivalence, pH = pK_a

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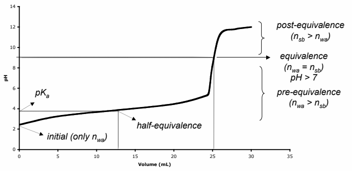
Weak Acid + Strong Base



Initial: $\mathrm{pH} = -\log\sqrt{K_a C_{wa}}$

Pre-equivalence: $\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{n_{sb}}{n_{wa} - n_{sb}}\right)$

Equivalence: $\mathrm{pH} = 14 + \log\sqrt{\left(\frac{K_w}{K_a}\right)\left(\frac{n_{wa}}{V_{wa} + V_{sb}}\right)}$

Post-equivalence: $\mathrm{pH} = 14 + \log\left(\frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right)$

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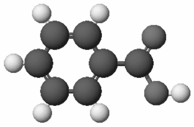
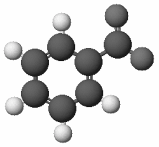
Acid-Base Reactions

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH of the initial solution? K_a = 6.3 x 10^{-5}**

$HBz + H_2O \rightleftharpoons Bz^- + H_3O^+$



$C_6H_5CO_2H$ = HBz
Benzoic acid



Benzoate ion = Bz^-

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Acid-Base Reactions

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH of the initial solution? K_a = 6.3 x 10^{-5}**

$HBz + H_2O \rightleftharpoons Bz^- + H_3O^+$

SOLUTION:

For weak acids,

$$\mathrm{pH} = -\log\sqrt{K_a C_{wa}}$$

$$\mathrm{pH} = -\log\sqrt{(6.3*10^{-5})(0.025)}$$

pH = 2.90

MAR

Acid-Base Reactions

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the** pH after 10. mL of NaOH **have been added? K_a = 6.3 x 10^{-5}**

$HBz + H_2O \rightleftharpoons Bz^- + H_3O^+$

SOLUTION:

First, determine which region **of a** weak acid **(benzoic acid) and** strong base **(NaOH)** titration **to use by *comparing mol HBz to mol NaOH***

n_{wa} = 0.100 L * 0.025 M = 0.0025 mol **HBz**

n_{sb} = 0.010 L * 0.100 M = 0.0010 mol **NaOH**

Since $n_{wa} > n_{sb}$, this pH will fall in the pre-equivalence region

***Note that* because n_{sb} is converted to mol Bz^- (the conjugate base), this region acts like a** buffer

MAR

Acid-Base Reactions

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the** pH after 10. mL of NaOH **have been added? K_a = 6.3 x 10^{-5}**

***From before:* n_{wa} = 0.0025 mol, n_{sb} = 0.0010 mol**

pK_a = -log K_a = - log (6.3*10^{-5}) = 4.20

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{n_{sb}}{n_{wa} - n_{sb}}\right)$$

A version of the Henderson-Hasselbalch equation!

$$\mathrm{pH} = 4.20 + \log\left(\frac{0.0010}{0.0025 - 0.0010}\right)$$

pH = 4.20 - 0.176 = 4.02

MAR

Acid-Base Reactions

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the** pH after 12.5 mL of NaOH **have been added? K_a = 6.3 x 10^{-5}**

***From before:* n_{wa} = 0.0025 mol, pK_a =** 4.20

n_{sb} = 0.0125 L * 0.100 M = 0.00125 mol NaOH

Since $n_{wa} > n_{sb}$, this is the pre-equivalence region

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{n_{sb}}{n_{wa} - n_{sb}}\right)$$

$$\mathrm{pH} = 4.20 + \log\left(\frac{0.00125}{0.0025 - 0.00125}\right) = 4.20 + \log(1)$$

pH = 4.20 + 0 = 4.20

MAR

Acid-Base Reactions

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the** pH after 12.5 mL of NaOH **have been added?** **K_a = 6.3 x 10^{-5}**

Before: n_{wa} **= 0.0025 mol,** pK_a **= 4.20,** n_{sb} **= 0.00125 mol**

When $n_{sb} = {}^1/_2 n_{wa}$, this is called the half-equivalence region

$pH = pK_a$ **at the half-equivalence point**

Useful method of finding K_a (and K_b) values

Also, **the volume of titrant (NaOH) at half equivalence is exactly half the volume necessary to reach equivalence**

We will need (2*12.5) = 25 mL **of NaOH to reach equivalence!**

Acid-Base Reactions

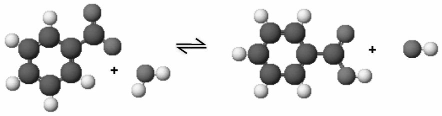
QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH to the** equivalence point**. What is the pH at the equivalence point?** **K_a = 6.3 x 10^{-5}**

At equivalence, **HBz + NaOH ---> Na^+ + Bz^- + H_2O**

mol NaOH = mol HBz, or *NaOH annihilates HBz*

mol HBz = mol Bz^- at equivalence, and *pH dominated by conjugate base of weak acid*

pH at equivalence point will be basic when titrating a weak acid with a strong base!



Acid-Base Reactions

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH to the** equivalence point**. What is the pH at the equivalence point?** **K_a = 6.3 x 10^{-5}**

n_{wa} **= 0.100 L * 0.025 M =** 0.0025 mol **HBz**

0.0025 mol HBz = 0.0025 mol NaOH *at equivalence*

0.0025 mol NaOH * (L / 0.100 mol) = 0.025 L = V_{sb}

$$pH = 14 + \log\sqrt{\left(\frac{K_w}{K_a}\right)\left(\frac{n_{wa}}{V_{wa}+V_{sb}}\right)}$$

$$pH = 14 + \log\sqrt{\left(\frac{10^{-14}}{6.3{*}10^{-5}}\right)\left(\frac{0.0025}{0.100+0.025}\right)}$$

pH = 14 + (-5.75) = 8.25

Acid-Base Reactions

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the** pH after 26.0 mL of NaOH **have been added?**

SOLUTION: *(from before, n_{wa} = 0.0025 mol)*

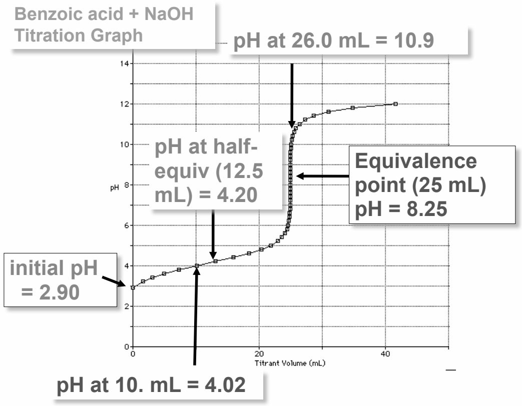
It took 25 mL of NaOH to reach equivalence; hence, we are now in the post-equivalence region

n_{sb} **= 0.100 M * 0.026 L =** 0.0026 mol

$$pH = 14 + \log\left(\frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right)$$

$$pH = 14 + \log\left(\frac{0.0026 - 0.0025}{0.026 + 0.100}\right)$$

pH = 14 + (-3.10) = 10.9



Benzoic acid + NaOH Titration Graph

pH at 26.0 mL = 10.9

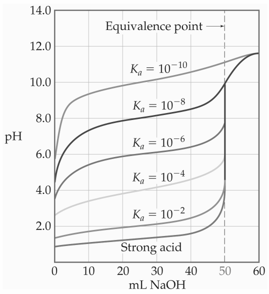
pH at half-equiv (12.5 mL) = 4.20

Equivalence point (25 mL) pH = 8.25

initial pH = 2.90

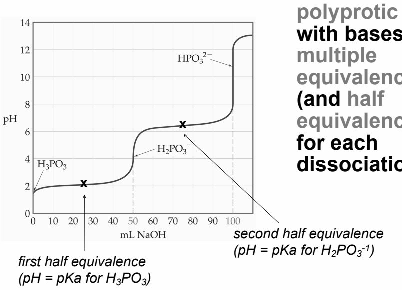
pH at 10. mL = 4.02

Acid-Base Reactions



With weaker acids, the initial pH is higher and pH changes near the equivalence point are more subtle.

Polyprotic Acids



second half equivalence (pH = pKa for $H_2PO_3^{-1}$)

first half equivalence (pH = pKa for H_3PO_3)

Titrations of polyprotic acids with bases have multiple equivalence points (and half equivalence points) for each dissociation.

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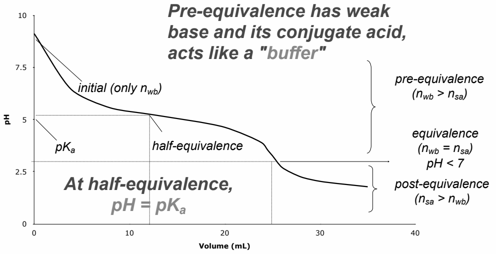
Weak Base + Strong Acid

Equivalence point dominated by conjugate acid of weak base

A weak base + strong acid titration



Pre-equivalence has weak base and its conjugate acid, acts like a "buffer"

At half-equivalence, pH = pK_a

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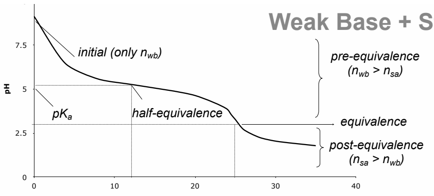
Weak Base + Strong Acid



Initial: $$pH = 14 + \log\sqrt{K_b C_{wb}}$$

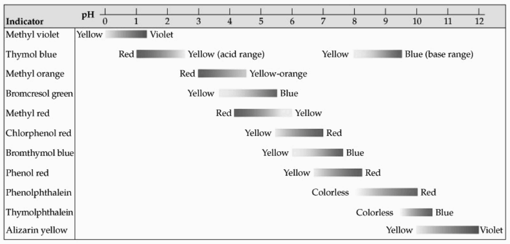
Pre-equivalence: $$pH = pK_a + \log\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right)$$

Equivalence: $$pH = -\log\sqrt{\left(\frac{K_w}{K_b}\right)\left(\frac{n_{wb}}{V_{wb} + V_{sa}}\right)}$$

Post-equivalence: $$pH = -\log\left(\frac{n_{sa} - n_{wb}}{V_{sa} + V_{wb}}\right)$$

MAR

pH Indicators



Indicator	pH 0 1 2 3 4 5 6 7 8 9 10 11 12
Methyl violet	Yellow ▨ Violet
Thymol blue	Red ▨ Yellow (acid range) Yellow ▨ Blue (base range)
Methyl orange	Red ▨ Yellow-orange
Bromcresol green	Yellow ▨ Blue
Methyl red	Red ▨ Yellow
Chlorphenol red	Yellow ▨ Red
Bromthymol blue	Yellow ▨ Blue
Phenol red	Yellow ▨ Red
Phenolphthalein	Colorless ▨ Red
Thymolphthalein	Colorless ▨ Blue
Alizarin yellow	Yellow ▨ Violet

Equivalence point important in titration, can use an indicator to signify equivalence point

Indicator color change must reflect equivalence point to be useful!

Focus on bromthymol blue for next slide

MAR

Color Changes for Bromthymol Blue

pH < 6.0 pH = 6.0-7.5 pH > 7.5

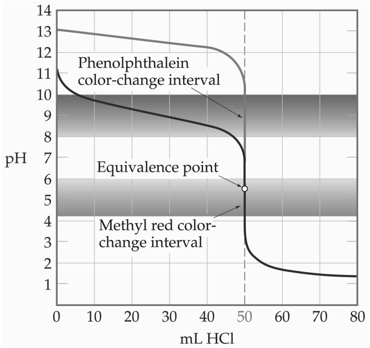
MAR

pH Indicators

Which indicator to use? Phenolphthalein or Methyl Red?

The pH at the equivalence point in this titration is < 7.

Methyl red is the indicator of choice here.

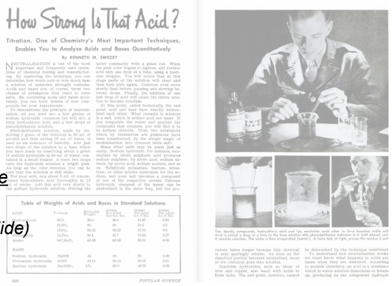


MAR

End of Chapter 14 Part II

See:

- *Chapter Fourteen Part II Study Guide*
- *Chapter Fourteen Part II Concept Guide*
- *Types of Equilibrium Constants*
- *Titration Guide*
- *Buffers and Henderson-Hasselbalch Guide*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*



How Strong Is That Acid?

Titration, One of Chemistry's Most Important Techniques, Enables You to Analyze Acids and Bases Quantitatively

By KENNETH M. SWEZEY

Important Equations, Constants, and Handouts from this Chapter:

Titrations (SA+SB, SB+SA, WA+SB, WB+SA) *and* **Buffers** *chapter*

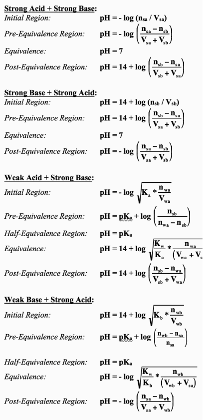
$$\mathbf{pH = pK_a + \log\frac{[Conj.\ base]}{[Acid]}}$$

$$pH = pK_a + \log\frac{\left(mol_{Conj\ base} - mol_{strong\ acid}\right)}{\left(mol_{weak\ acid} + mol_{strong\ acid}\right)}$$

$$pH = pK_a + \log\frac{\left(mol_{Conj\ base} + mol_{strong\ base}\right)}{\left(mol_{weak\ acid} - mol_{strong\ base}\right)}$$

Handouts:

- *Manipulating Equilibrium Constant Expressions*
- *Types of Equilibrium Constants*
- *Table of K_a and K_b values in Problem Set #2*
- *Titration Guide*
- *Buffers and Henderson-Hasselbalch Guide*



Strong Acid + Strong Base:

Initial Region: $pH = -\log(n_{sa} / V_{sa})$

Pre-Equivalence Region: $pH = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

Equivalence: $pH = 7$

Post-Equivalence Region: $pH = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$

Strong Base + Strong Acid:

Initial Region: $pH = 14 + \log(n_{sb} / V_{sb})$

Pre-Equivalence Region: $pH = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right)$

Equivalence: $pH = 7$

Post-Equivalence Region: $pH = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

Weak Acid + Strong Base:

Initial Region: $pH = -\log\sqrt{K_a * \frac{n_{wa}}{V_{wa}}}$

Pre-Equivalence Region: $pH = pK_a + \log\left(\frac{n_{sb}}{n_{wa} - n_{sb}}\right)$

Half-Equivalence Region: $pH = pK_a$

Equivalence: $pH = 14 + \log\sqrt{\frac{K_w}{K_a} * \frac{n_{wa}}{(V_{wa} + V_{s}}}$

Post-Equivalence Region: $pH = 14 + \log\left(\frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right)$

Weak Base + Strong Acid:

Initial Region: $pH = 14 + \log\sqrt{K_b * \frac{n_{wb}}{V_{wb}}}$

Pre-Equivalence Region: $pH = pK_a + \log\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right)$

Half-Equivalence Region: $pH = pK_a$

Equivalence: $pH = -\log\sqrt{\frac{K_w}{K_b} * \frac{n_{wb}}{(V_{wb} + V_{sa})}}$

Post-Equivalence Region: $pH = -\log\left(\frac{n_{sa} - n_{wb}}{V_{sa} + V_{wb}}\right)$

End of Chapter Problems: *Test Yourself*

See practice problem set #3 for additional titration and buffer examples

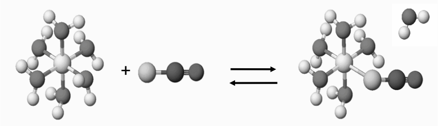
1. Does the pH of the solution increase, decrease, or stay the same when you: a) Add solid ammonium chloride to a dilute aqueous solution of NH_3; b) Add solid sodium acetate to a dilute aqueous solution of acetic acid; c) Add solid NaCl to a dilute aqueous solution of NaOH?
2. For each of the following cases, decide whether the pH is less than 7, equal to 7, or greater than 7: a) equal volumes of 0.10 M acetic acid, CH_3CO_2H, and 0.10 M KOH are mixed; b) 25 mL of 0.015 M NH_3 is mixed with 25 mL of 0.015 M HCl; c) 150 mL of 0.20 M HNO_3 is mixed with 75 mL of 0.40 M NaOH
3. What is the pH of a solution that consists of 0.20 M ammonia, NH_3, and 0.20 M ammonium chloride, NH_4Cl? ($K_a = 5.6 \times 10^{-10}$)
4. What mass of sodium acetate, $NaCH_3CO_2$, must be added to 1.00 L of 0.10 M acetic acid to give a solution with a pH of 4.50? ($K_a = 1.8 \times 10^{-5}$)
5. Phenol, C_6H_5OH, is a weak organic acid. Suppose 0.515 g of the compound is dissolved in exactly 125 mL of water. The resulting solution is titrated with 0.123 M NaOH: $\mathbf{C_6H_5OH(aq) + OH^{-1}(aq) \rightleftarrows C_6H_5O^{-1}(aq) + H_2O(l)}$ a) What is the pH of the original solution of phenol? b) What are the concentrations of all of the following ions at the equivalence point: Na^{+1}, H_3O^{+1}, OH^{-1}, and $C_6H_5O^{-1}$? c) What is the pH of the solution at the equivalence point?

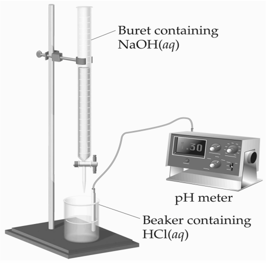
End of Chapter Problems: *Answers*

1. a) pH decreases; b) pH increases; c) no change to pH
2. a. pH > 7 b. pH < 7 c. pH = 7
3. pH = 9.25
4. 4.7 g
5. a) pH = 5.62 b) $[Na^{+1}] = 3.23 \times 10^{-2}$ mol/L, $[H_3O^{+1}] = 6.5 \times 10^{-12}$ mol/L, $[OH^{-1}] = 1.5 \times 10^{-3}$ mol/L, and $[C_6H_5O^{-1}] = 3.07 \times 10^{-2}$ mol/L c) pH = 11.19

See practice problem set #3 for additional titration and buffer examples

Chemistry 223 Exam I Review
Chapters 13 and 14 ("Part I & II")





Chemistry 223
Professor Michael Russell

Last update: 4/29/24

We place 0.010 mol of $N_2O_4(g)$ in a 2.0 L flask at 200 °C. After reaching equilibrium, $[N_2O_4] = 0.0038$ M. Calculate K_c for the following reaction:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

A. 1600
B. 1.5×10^{-3}
C. 6.1×10^{-4}
D. 8.8×10^{-6}
E. -3.1×10^{-3}

Given the following two equilibria:

$NiCO_3(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$ $K_1 = 6.6 \times 10^{-9}$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$ $K_2 = 4.8 \times 10^{-11}$

calculate the equilibrium constant for the following reaction:

$NiCO_3(s) + H_3O^+(aq) \rightleftharpoons Ni^{2+}(aq) + HCO_3^-(aq) + H_2O(l)$

A. 7.3×10^{-3}
B. 3.2×10^{-19}
C. 140
D. 1.8×10^{-9}
E. 1100

$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$, $K_c = 54.3$

Initially, $[H_2] = 0.00623$ M, $[I_2] = 0.00414$ M, and $[HI] = 0.0424$ M. Find the equilibrium concentrations.

A. $[H_2] = 0.00201$ M, $[I_2] = 0.00112$ M, $[HI] = 0.0643$ M
B. $[H_2] = 0.00222$ M, $[I_2] = 0.00168$ M, $[HI] = 0.0112$ M
C. $[H_2] = 0.00917$ M, $[I_2] = 0.00667$ M, $[HI] = 0.0212$ M
D. $[H_2] = 0.00676$ M, $[I_2] = 0.00467$ M, $[HI] = 0.0414$ M
E. $[H_2] = 0.00623$ M, $[I_2] = 0.00414$ M, $[HI] = 0.0424$ M

$\Delta H^o = -18.8$ kJ, $K_c = 10.5$, for:

$$2\ CH_2Cl_2(g) \rightleftharpoons CH_4(g) + CCl_4(g)$$

If the temperature on the equilibrium system is suddenly decreased, the value of K_c:

A. increases
B. decreases
C. remains the same

You add 0.535 g of NaOH (MM = 40.0 g mol^{-1}) to 100.0 mL of water at 25 °C. What is $[H_3O^+]$ in this solution?

A. 0.134 M
B. 7.48×10^{-14} M
C. 1.34×10^{13} M
D. 6.87×10^{-12} M

Considering only H_2S ($K_a = 1 \times 10^{-7}$) and HCN ($K_a = 4 \times 10^{-10}$), predict in which direction the following equilibrium lies:

$$HCN(aq) + HS^-(aq) \rightleftharpoons CN^-(aq) + H_2S(aq)$$

A. equilibrium lies to the left
B. equilibrium lies to the right
C. equilibrium is perfectly balanced left and right
D. cannot be determined

MAR

What is $[H_3O^+]$ in a 0.10 M solution of HCN at 25 °C? (K_a for HCN = 4.0×10^{-10})

A. 1.6×10^{-9} M
B. 6.3×10^{-6} M
C. 2.0×10^{-5} M
D. 4.0×10^{-11} M
E. 0.10 M

MAR

In a 0.15 M solution of Na_2CO_3, what are $[H_3O^+]$, $[OH^-]$ and the pH? K_b for CO_3^{2-} is 2.1×10^{-4}.

	$[H_3O^+]$	$[OH^-]$	pH
A.	5.6×10^{-3}	1.8×10^{-12}	5.61
B.	1.8×10^{-12}	5.6×10^{-3}	11.75
C.	5.6×10^{-3}	1.8×10^{-12}	11.75
D.	1.8×10^{-12}	5.6×10^{-3}	5.61

MAR

Place the following acids in order of increasing acid strength.

(a) Anilinium ion, $pK_a = 4.60$
(b) Benzilic acid, $pK_a = 3.09$
(c) Chloroacetic acid, $pK_a = 2.98$
(d) Dibromophenol, $pK_a = 8.06$

A. a, b, c, d
B. d, c, b, a
C. c, b, a, d
D. d, a, b, c
E. a, c, d, c

MAR

Classify the following as ***Lewis*** acids or bases.

BH_3, NH_3, Cl^{-1}, Al^{3+}, Cr^{3+}

A. acid, base, base, acid, acid
B. base, base, base, acid, acid
C. base, acid, acid, base, base
D. acid, base, acid, base, base
E. Public Enemy is #1!

MAR

You have a solution of NH_4Cl. What effect will addition of NH_3 have on the pH of the solution?

A. increase pH
B. no effect
C. decrease pH
D. cannot tell from information given

MAR

You have a solution of NH_4Cl. What effect will addition of NaCl have on the pH of the solution?

A. increase pH
B. no effect
C. decrease pH
D. cannot tell from information given

MAR

Which choice would be an ideal buffer solution?

A. 0.20 M HCN and 0.10 M KCN
B. 0.20 M HCl and 0.10 M KOH
C. 0.20 M CH_3CO_2H and 0.10 M HCO_2H
D. 0.10 HCl and 0.010 M KCl
E. 0.10 M CH_3OH and 0.10 M NaOH

MAR

What is the pH of a buffer that is composed of 0.20 M NH_4Cl and 0.20 M NH_3? (K_a for NH_4^+ = 5.6×10^{-10})

A. 4.85
B. 5.65
C. 7.00
D. 9.25
E. 10.05

MAR

What is the pH of a buffer that is composed of 0.20 M NH_4Cl and 0.50 M NH_3? (K_a for NH_4^+ = 5.6×10^{-10})

A. 4.75
B. 5.65
C. 7.00
D. 9.25
E. 9.65

MAR

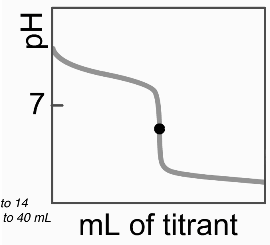
What volume of 0.10 M sodium acetate must be added to 100. mL of 0.10 M acetic acid (K_a = 1.8×10^{-5}) to have a pH of 4.00?

A. 100. mL
B. 50. mL
C. 36 mL
D. 18 mL
E. 9.0 mL

MAR

What type of titration does the graph below represent?

A. strong acid + strong base
B. strong base + strong acid
C. weak acid + strong base
D. weak base + strong acid
E. weak base + weak acid



pH scale: from 0 to 14
Volume scale: from 0 to 40 mL

MAR

You mix 15.0 mL of 0.400 M HCl with 15.0 mL of 0.400 M NH_3. What is the pH of the resulting solution? ($K_b = 1.8 \times 10^{-5}$)

A. 11.43
B. 9.26
C. 7.00
D. 5.54
E. 4.98

MAR

0.40 g of NaOH (MM = 40. g/mol) are mixed with 100 mL of 0.10 M acetic acid. What is the pH of the resulting solution? ($K_a = 1.8 \times 10^{-5}$)

A. 1.00
B. 2.87
C. 7.00
D. 8.87
E. 13.00

MAR

What is the pH of the solution when 50. mL of 0.10 M HCl and 100. mL of 0.10 M NaCN are mixed? $K_a(HCN) = 4.0 \times 10^{-10}$

A. 8.65
B. 8.80
C. 5.20
D. 5.35
E. 9.40

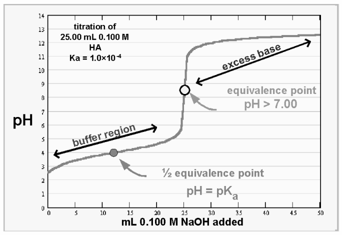
MAR

Add 40. mL of 0.50 M NaOH to 50.0 mL of 1.00 M NH_4Cl. What is the pH of the resulting solution? $K_b(NH_3) = 1.8 \times 10^{-5}$

A. 4.56
B. 4.74
C. 7.00
D. 9.08
E. 10.70

MAR

End of Review - *good luck with your studying!*



Need more practice?

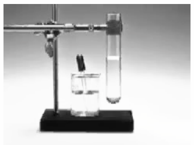
- *Practice Problem Sets (online)*
- *Concept Guides (Companion and online)*
- *Chapter Guides (online)*
- *End of Chapter Problems in Textbook (every other question has answer at end)*

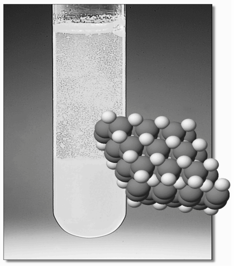
Good luck with your studying!

MAR

PRECIPITATION REACTIONS

Chapter 15

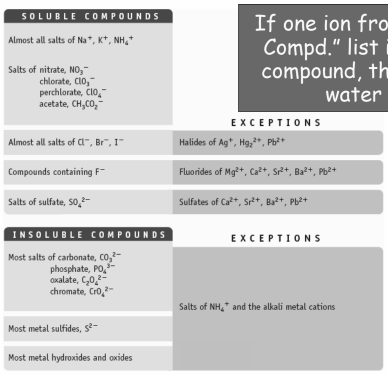




Chemistry 223
Professor Michael Russell

Last update: 4/29/24

Flashback - Aqueous Salts!



SOLUBLE COMPOUNDS	EXCEPTIONS
Almost all salts of Na^+, K^+, NH_4^+	
Salts of nitrate, NO_3^- chlorate, ClO_3^- perchlorate, ClO_4^- acetate, $CH_3CO_2^-$	
Almost all salts of Cl^-, Br^-, I^-	Halides of Ag^+, Hg_2^{2+}, Pb^{2+}
Compounds containing F^-	Fluorides of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}
Salts of sulfate, SO_4^{2-}	Sulfates of Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}

INSOLUBLE COMPOUNDS	EXCEPTIONS
Most salts of carbonate, CO_3^{2-} phosphate, PO_4^{3-} oxalate, $C_2O_4^{2-}$ chromate, CrO_4^{2-}	Salts of NH_4^+ and the alkali metal cations
Most metal sulfides, S^{2-}	
Most metal hydroxides and oxides	

If one ion from the "Soluble Compd." list is present in a compound, the compound is water soluble.

$Ba(NO_3)_2(aq)$?
soluble

$BaCl_2(aq)$?
soluble

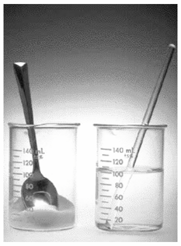
$BaSO_4(aq)$?
insoluble, $BaSO_4(s)$

Solubility of a Salt

Consider NaCl dissolving in water:

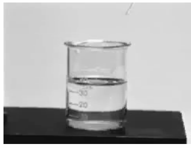
$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$

Solubility of NaCl exceeded when solid precipitate does not dissolve



Analysis of Silver Group

Ag^+ Pb^{2+} Hg_2^{2+}
⇩
AgCl $PbCl_2$ Hg_2Cl_2



All salts formed in this experiment are said to be INSOLUBLE

They form when mixing moderately concentrated solutions of the metal ion with chloride ions.

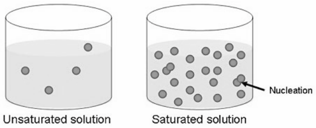
Analysis of Silver Group

Ag^+ Pb^{2+} Hg_2^{2+}
⇩
AgCl $PbCl_2$ Hg_2Cl_2

Although all salts formed in this experiment are said to be insoluble, they do dissolve to some SLIGHT extent.

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

When equilibrium has been established, no more AgCl dissolves and the solution is SATURATED.



Analysis of Silver Group

Ag^+ Pb^{2+} Hg_2^{2+}
⇩
AgCl $PbCl_2$ Hg_2Cl_2

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

When solution is SATURATED, expt. shows that $[Ag^+] = 1.67 \times 10^{-5}$ M.

This is equivalent to the **SOLUBILITY** of AgCl.

What is $[Cl^-]$?

This is also equivalent to the AgCl solubility, so **$[Cl^-] = 1.67 \times 10^{-5}$ M**

Ag^+ Pb^{2+} Hg_2^{2+}

⇩

$AgCl$ $PbCl_2$ Hg_2Cl_2

Analysis of Silver Group

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

Saturated solution has

$[Ag^+] = [Cl^-] = 1.67 \times 10^{-5}$ M

Use this to calculate K_c

$K_c = [Ag^+] [Cl^-]$

$= (1.67 \times 10^{-5})(1.67 \times 10^{-5})$

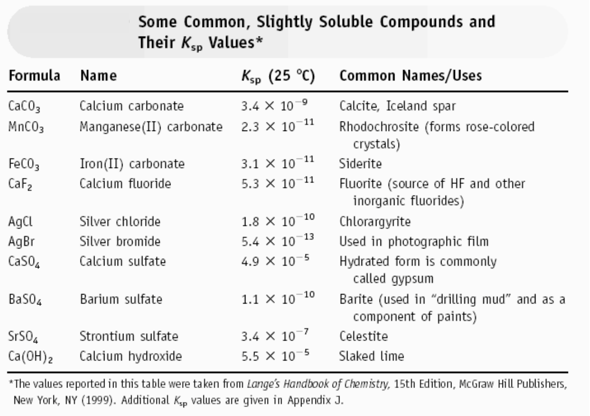
$= \boxed{2.79 \times 10^{-10}}$

This type of K_c is the product of "solubilities", we call it

K_{sp} = solubility product constant

See: Solubility Guide

MAR



Some Common, Slightly Soluble Compounds and Their K_{sp} Values*

Formula	Name	K_{sp} (25 °C)	Common Names/Uses
$CaCO_3$	Calcium carbonate	3.4×10^{-9}	Calcite, Iceland spar
$MnCO_3$	Manganese(II) carbonate	2.3×10^{-11}	Rhodochrosite (forms rose-colored crystals)
$FeCO_3$	Iron(II) carbonate	3.1×10^{-11}	Siderite
CaF_2	Calcium fluoride	5.3×10^{-11}	Fluorite (source of HF and other inorganic fluorides)
AgCl	Silver chloride	1.8×10^{-10}	Chlorargyrite
AgBr	Silver bromide	5.4×10^{-13}	Used in photographic film
$CaSO_4$	Calcium sulfate	4.9×10^{-5}	Hydrated form is commonly called gypsum
$BaSO_4$	Barium sulfate	1.1×10^{-10}	Barite (used in "drilling mud" and as a component of paints)
$SrSO_4$	Strontium sulfate	3.4×10^{-7}	Celestite
$Ca(OH)_2$	Calcium hydroxide	5.5×10^{-5}	Slaked lime

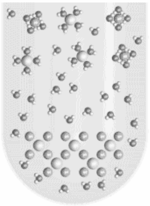
*The values reported in this table were taken from *Lange's Handbook of Chemistry*, 15th Edition, McGraw Hill Publishers, New York, NY (1999). Additional K_{sp} values are given in Appendix J.

MAR

Lead(II) Chloride

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq)$

$K_{sp} = 1.9 \times 10^{-5}$



MAR

Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ I^-(aq)$

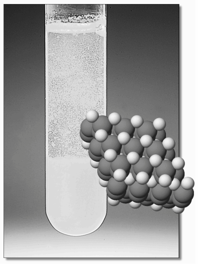
Calculate K_{sp} if solubility = 0.00130 M

Solution

Solubility **refers to how many moles of** *solid dissolve per L*

1. **Solubility = $[Pb^{2+}]$ = 1.30×10^{-3} M**

$[I^-] = 2 \times [Pb^{2+}] = 2.60 \times 10^{-3}$ M



MAR

Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ I^-(aq)$

Calculate K_{sp} if solubility = 0.00130 M

Solution

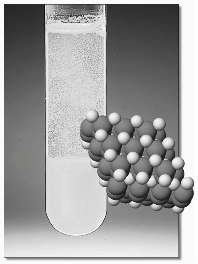
1. **Solubility = $[Pb^{2+}]$ = 1.30×10^{-3} M**

$[I^-] = 2 \times [Pb^{2+}] = 2.60 \times 10^{-3}$ M

2. $K_{sp} = [Pb^{2+}] [I^-]^2$

$= [Pb^{2+}] \{2 \bullet [Pb^{2+}]\}^2$

$= 4 [Pb^{2+}]^3$



MAR

Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ I^-(aq)$

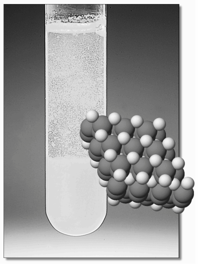
Calculate K_{sp} if solubility = 0.00130 M

Solution

2. $K_{sp} = 4[Pb^{2+}]^3 = 4(\text{solubility})^3$

$K_{sp} = 4\ (1.30 \times 10^{-3})^3 = 8.79 \times 10^{-9}$

Notice that solubility of PbI_2 (x) and K_{sp} related here by: $K_{sp} = 4x^3$



MAR

Solubility and K_{sp} Relations

# cations	*# anions*	*K_{sp} and solubility (x)*	*Examples*
1	1	$K_{sp} = x^2$ $x = (K_{sp})^{1/2}$	**NaCl, SrO, $KClO_3$**
1	2	$K_{sp} = 4x^3$ $x = (K_{sp}/4)^{1/3}$	**PbI_2, $Mg(OH)_2$**
2	1	$K_{sp} = 4x^3$ $x = (K_{sp}/4)^{1/3}$	**Na_2O, $(NH_4)_2SO_3$**
3	1	$K_{sp} = 27x^4$ $x = (K_{sp}/27)^{1/4}$	**Li_3P, $(NH_4)_3PO_4$**
1	3	$K_{sp} = 27x^4$ $x = (K_{sp}/27)^{1/4}$	**$AlBr_3$, $Cr(NO_3)_3$**
2	3	$K_{sp} = 108x^5$ $x = (K_{sp}/108)^{1/5}$	**Fe_2O_3, $Al_2(SO_4)_3$**
3	2	$K_{sp} = 108x^5$ $x = (K_{sp}/108)^{1/5}$	**Ti_3As_2, $Mg_3(PO_4)_2$**

See: Solubility Guide

Solubility and K_{sp} Relations

Example: **What is the solubility of copper(II) phosphate if $K_{sp} = 1.4*10^{-37}$?**

Answer: Formula = $Cu_3(PO_4)_2$

3 cations & 2 anions, so $K_{sp} = 108x^5$

$x = (1.4*10^{-37}/108)^{(1/5)} = \mathbf{1.7*10^{-8}\ M}$

Example: **What is K_{sp} for magnesium carbonate if the solubility at 25 ˚C is $2.6*10^{-3}$ M?**

Answer: Formula = $MgCO_3$,

1 cation & 1 anion, so $K_{sp} = x^2$

$K_{sp} = (2.6*10^{-3})^2 = \mathbf{6.8*10^{-6}}$

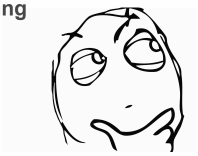
Precipitating an Insoluble Salt

$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\ Cl^-(aq)$

$K_{sp} = 1.1 \times 10^{-18} = [Hg_2^{2+}]\ [Cl^-]^2$

If $[Hg_2^{2+}] = 0.010$ M, what $[Cl^-]$ is req'd to just begin the precipitation of Hg_2Cl_2?

That is, what is the maximum $[Cl^-]$ that can be in solution with 0.010 M Hg_2^{2+} without forming Hg_2Cl_2?



Precipitating an Insoluble Salt

$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\ Cl^-(aq)$

$K_{sp} = 1.1 \times 10^{-18} = [Hg_2^{2+}]\ [Cl^-]^2$

Solution

$[Cl^-]$ that can exist when $[Hg_2^{2+}] = 0.010$ M:

$$[Cl^-] = \sqrt{\frac{K_{sp}}{0.010}} = 1.0 \times 10^{-8}\ M$$

If this conc. of Cl^- is just exceeded, Hg_2Cl_2 begins to precipitate.

Precipitating an Insoluble Salt

$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\ Cl^-(aq)$

$K_{sp} = 1.1 \times 10^{-18}$

Now raise $[Cl^-]$ to 1.0 M when $[Hg_2^{2+}] = 0.010$ M. What is the value of $[Hg_2^{2+}]$ at this point?

Solution

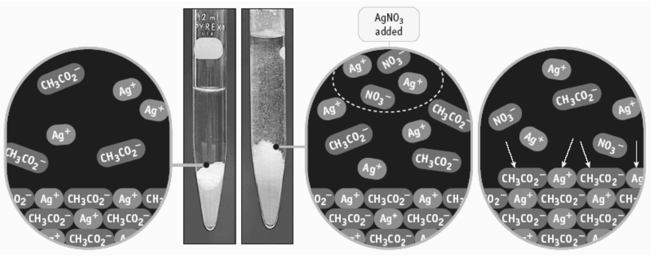
$[Hg_2^{2+}] = K_{sp} / [Cl^-]^2$

$= K_{sp} / (1.0)^2 = 1.1 \times 10^{-18}$ M

The concentration of Hg_2^{2+} has been reduced by 10^{16}!

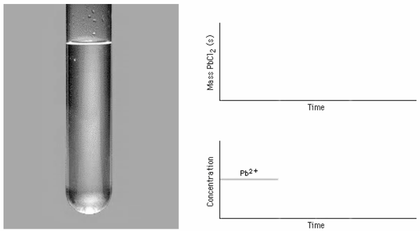
The Common Ion Effect

Adding an ion "common" to an equilibrium causes the equilibrium to shift back to reactant.



Common Ion Effect

Adding an Ion "Common" to an Equilibrium



$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq)$

MAR

The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\ [SO_4^{2-}]$

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

Solution: (part a)

Solubility in pure water = $[Ba^{2+}] = [SO_4^{2-}] = x$

$K_{sp} = [Ba^{2+}]\ [SO_4^{2-}] = x^2$

$x = (K_{sp})^{1/2} = 1.0 \times 10^{-5}$ M

Note 1:1 ratio of cation to anion: $K_{sp} = x^2$

MAR

The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\ [SO_4^{2-}]$

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

Solution: (part b)

So... **Solubility in pure water = 1.0×10^{-5} mol/L.**

Now **dissolve $BaSO_4$ in water already containing 0.010 M Ba^{2+}.**

Which way will the "common ion" shift the equilibrium? ___ Will solubility of $BaSO_4$ be less than or greater than in pure water?___

MAR

The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\ [SO_4^{2-}]$

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

Solution: (part b)

	$[Ba^{2+}]$	**$[SO_4^{2-}]$**
initial		
change		
equilib.		

MAR

The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\ [SO_4^{2-}]$

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

Solution: (part b)

$K_{sp} = [Ba^{2+}]\ [SO_4^{2-}] = (0.010 + y)\ (y)$

Because $y < 1.0 \times 10^{-5}$ M (= x, the solubility in pure water), this means 0.010 + y is about equal to 0.010. Therefore,

$K_{sp} = 1.1 \times 10^{-10} = (0.010)(y)$

$y = 1.1 \times 10^{-8}$ M = solubility *in presence of added Ba^{2+} ion.*

MAR

The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\ [SO_4^{2-}]$

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

Solution:

Solubility in pure water = x = 1.0×10^{-5} M

Solubility in presence of added Ba^{2+}
= 1.1×10^{-8} M

Le Chatelier's Principle is followed!

See: Solubility Guide

MAR

DISTRACTIONS!!!

MAR

Separating Metal Ions

Cu^{2+}, Ag^{+}, Pb^{2+}

	K_{sp} Values
AgCl	1.8×10^{-10}
$PbCl_2$	1.7×10^{-5}
$PbCrO_4$	1.8×10^{-14}

MAR

Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and 0.020 M Pb^{2+}. Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow $PbCrO_4$. Which precipitates first?

K_{sp} for $Ag_2CrO_4 = 9.0 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}]$

K_{sp} for $PbCrO_4 = 1.8 \times 10^{-14} = [Pb^{2+}] [CrO_4^{2-}]$

Solution

The substance whose K_{sp} is first exceeded precipitates first.

The ion requiring the lesser amount of CrO_4^{2-} ppts. first.

MAR

Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and 0.020 M Pb^{2+}. Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow $PbCrO_4$. Which precipitates first?

K_{sp} for $Ag_2CrO_4 = 9.0 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}]$

K_{sp} for $PbCrO_4 = 1.8 \times 10^{-14} = [Pb^{2+}] [CrO_4^{2-}]$

Solution - Calculate $[CrO_4^{2-}]$ required by each ion

$[CrO_4^{2-}]$ to ppt. $Ag_2CrO_4 = K_{sp} / [Ag^+]^2$

$= 9.0 \times 10^{-12} / (0.020)^2 = 2.3 \times 10^{-8}$ M

$[CrO_4^{2-}]$ to ppt. $PbCrO_4 = K_{sp} / [Pb^{2+}]$

$= 1.8 \times 10^{-14} / 0.020 = 9.0 \times 10^{-13}$ M

$PbCrO_4$ precipitates first.

MAR

Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and 0.020 M Pb^{2+}. Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow $PbCrO_4$. $PbCrO_4$ ppts. first.

K_{sp} $(Ag_2CrO_4) = 9.0 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}]$

K_{sp} $(PbCrO_4) = 1.8 \times 10^{-14} = [Pb^{2+}] [CrO_4^{2-}]$

How much Pb^{2+} remains in solution when Ag^+ begins to precipitate (at 2.3×10^{-8} M)?

Solution

We know that $[CrO_4^{2-}] = 2.3 \times 10^{-8}$ M to begin to precipitate Ag_2CrO_4.

What is the Pb^{2+} conc. at this point?

MAR

Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and 0.020 M Pb^{2+}. Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow $PbCrO_4$.

K_{sp} $(Ag_2CrO_4) = 9.0 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}]$

K_{sp} $(PbCrO_4) = 1.8 \times 10^{-14} = [Pb^{2+}] [CrO_4^{2-}]$

How much Pb^{2+} remains in solution when Ag^+ begins to precipitate (at 2.3×10^{-8} M)?

Solution

$[Pb^{2+}] = K_{sp} / [CrO_4^{2-}] = 1.8 \times 10^{-14} / 2.3 \times 10^{-8}$ M

$= 7.8 \times 10^{-7}$ M

Lead ion has dropped from 0.020 M to $< 10^{-6}$ M

MAR

Formation Constants

Complex Ions are systems with Lewis bases connected around the (Lewis) acidic metal center.

Examples: **$Zn(NH_3)_4^{2+}$, $Ag(CN)_2^{-1}$**

Can write a Formation Constant, K_f

$Ag^+(aq) + 2\ CN^{-1}(aq) \rightleftharpoons Ag(CN)_2^{-1}(aq)$, *and*

$$K_f = \frac{[Ag(CN)_2^{-1}]}{[Ag^+][CN^{-1}]^2} = 5.6 * 10^{18}$$

K_f values usually quite large (product-favored) and product is *always* the complex ion

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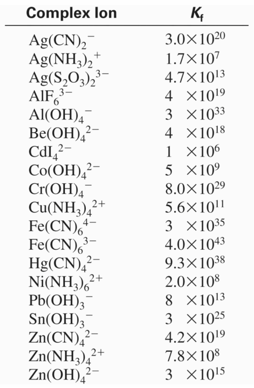
Formation Constants (K_f) at 25 °C



Complex Ion	K_f
$Ag(CN)_2^-$	3.0×10^{20}
$Ag(NH_3)_2^+$	1.7×10^{7}
$Ag(S_2O_3)_2^{3-}$	4.7×10^{13}
AlF_6^{3-}	4×10^{19}
$Al(OH)_4^-$	3×10^{33}
$Be(OH)_4^{2-}$	4×10^{18}
CdI_4^{2-}	1×10^{6}
$Co(OH)_4^{2-}$	5×10^{9}
$Cr(OH)_4^-$	8.0×10^{29}
$Cu(NH_3)_4^{2+}$	5.6×10^{11}
$Fe(CN)_6^{4-}$	3×10^{35}
$Fe(CN)_6^{3-}$	4.0×10^{43}
$Hg(CN)_4^{2-}$	9.3×10^{38}
$Ni(NH_3)_6^{2+}$	2.0×10^{8}
$Pb(OH)_3^-$	8×10^{13}
$Sn(OH)_3^-$	3×10^{25}
$Zn(CN)_4^{2-}$	4.2×10^{19}
$Zn(NH_3)_4^{2+}$	7.8×10^{8}
$Zn(OH)_4^{2-}$	3×10^{15}

Example:

$Ag^+(aq) + 2\ CN^{-1}(aq) \rightleftharpoons Ag(CN)_2^{-1}(aq)$

- **ions are** reactants
- **complex ion is** product
- **usually written as** net ionic reactions

MAR

Formation Constants

Complex Ions **can be helpful when dissolving solids.** *Ex:* **$AgCl(s)$ and $Ag(NH_3)_2^+(aq)$**

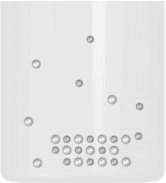
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ K_{sp}

$Ag^+(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$ K_f

----

$AgCl_{(s)} + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$

$K_{net} = K_{sp} * K_f$



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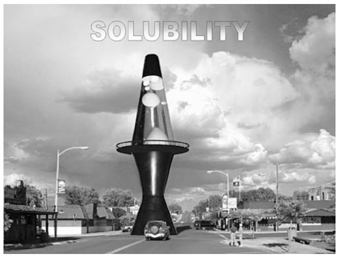
End of Chapter 15

See:

- *Chapter Fifteen Study Guide*
- *Chapter Fifteen Concept Guide*
- *Types of Equilibrium Constants*
- *Solubility Guide*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*



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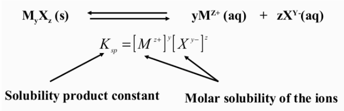
Important Equations, Constants, and Handouts from this Chapter:



$$M_yX_z(s) \rightleftharpoons yM^{Z+}(aq) + zX^{Y-}(aq)$$

$$K_{sp} = [M^{z+}]^y[X^{y-}]^z$$

Solubility product constant

Molar solubility of the ions

- *know how to* **predict solubility** *using* **CH 221 solubility guide**

$Ag^+(aq) + 2\ CN^{-1}(aq) \rightleftharpoons Ag(CN)_2^{-1}(aq)$

$$K_f = \frac{[Ag(CN)_2^{-1}]}{[Ag^+][CN^{-1}]^2} = 5.6 * 10^{18}$$

Solubility: **Common ion effect, separating salts by differences in solubility**

Handouts:

- *Types of Equilibrium Constants*
- *Solubility Guide*

MAR

End of Chapter Problems: ***Test Yourself***

1. Predict whether each of the following is insoluble or soluble in water: $(NH_4)_2CO_3$, $ZnSO_4$, NiS, $BaSO_4$
2. When 1.55 g of solid thallium(I) bromide is added to 1.00 L of water, the salt dissolves to a small extent: $TlBr(s) \rightleftharpoons Tl^+(aq) + Br^{-1}(aq)$ The thallium(I) and bromide ions in equilibrium with TlBr each have a concentration of 1.9×10^{-3} M. What is the value of K_{sp} for TlBr?
3. You add 0.979 g of $Pb(OH)_2$ to 1.00 L of pure water at 25 °C. The pH is 9.15. Estimate the value of K_{sp} for $Pb(OH)_2$.
4. Estimate the solubility of calcium fluoride, CaF_2, (a) in moles per liter and (b) in grams per liter of pure water. **$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^{-1}(aq)$** $K_{sp} = 5.3 \times 10^{-11}$
5. The K_{sp} value for radium sulfate, $RaSO_4$, is 3.7×10^{-11}. If 0.25 mg of radium sulfate is placed in 1.00×10^2 mL of water, does all of it dissolve? If not, how much dissolves? **$RaSO_4(s) \rightleftharpoons Ra^{2+}(aq) + SO_4^{-2}(aq)$**
6. Which compound is more soluble: $PbCl_2$ ($K_{sp} = 1.7 \times 10^{-5}$) or $PbBr_2$ ($K_{sp} = 6.6 \times 10^{-6}$)?

MAR

End of Chapter Problems: *Answers*

1. $(NH_4)_2CO_3$ & $ZnSO_4$ (soluble), NiS & $BaSO_4$ (insoluble)
2. $K_{sp} = 3.6 \times 10^{-6}$
3. $K_{sp} = 1.4 \times 10^{-15}$
4. a) 2.4×10^{-4} M b) 0.018 g/L
5. 0.05 mg does not dissolve
6. $PbCl_2$

MAR

Chemical Thermodynamics

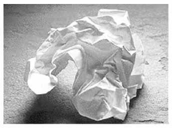
Chapter 16

Chemistry 223
Professor Michael Russell

Last update: 4/29/24

MAR

Thermodynamics and Kinetics

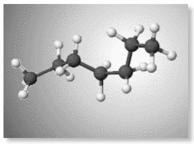


How to predict if a reaction can occur, given enough time?

THERMODYNAMICS

How to predict if a reaction can occur at a reasonable rate?

KINETICS



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First Law of Thermodynamics

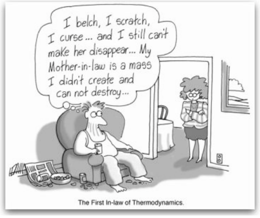
First Law of Thermodynamics: ***"Energy cannot be created or destroyed"*** **- conservation of energy**

The total energy of the universe cannot change though you can transfer it from one place to another

$\Delta E_{universe} = 0 = \Delta E_{system} + \Delta E_{surroundings}$

ΔE lost or gained through **heat** (q) and/or **work** (w)

Chemists focus on heat more than work; heat at constant pressure equals **enthalpy** (ΔH)



The First In-law of Thermodynamics.

MAR

Enthalpy - *CH 221 flashback!*

Enthalpy, ΔH, generally in kJ/mol

If products more stable than reactants, energy released

exothermic and ΔH = ***negative***

If reactants more stable than products, energy absorbed

endothermic and ΔH = ***positive***

Review **Hess' Law, $\Delta H°_{rxn} = \Sigma(\Delta H°_{prod}) - \Sigma(\Delta H°_{react})$, bond enthalpies**

Bond enthalpies (CH 222)

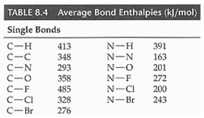
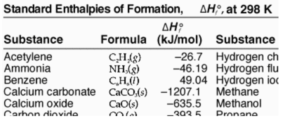


TABLE 8.4 Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391
C—C	348	N—N	163
C—N	293	N—O	201
C—O	358	N—F	272
C—F	485	N—Cl	200
C—Cl	328	N—Br	243
C—Br	276		

Formation enthalpies (CH 221)



Standard Enthalpies of Formation, $\Delta H_f°$, at 298 K

Substance	Formula	$\Delta H_f°$ (kJ/mol)	Substance
Acetylene	$C_2H_2(g)$	–26.7	Hydrogen ch
Ammonia	$NH_3(g)$	–46.19	Hydrogen flu
Benzene	$C_6H_6(l)$	49.04	Hydrogen ioc
Calcium carbonate	$CaCO_3(s)$	–1207.1	Methane
Calcium oxide	$CaO(s)$	–635.5	Methanol
Carbon dioxide	$CO_2(g)$	–393.5	Propane

MAR

Spontaneous Reactions

Thermodynamics asks if a reaction will occur under the given conditions; if it does, system is favored to react - a *product-favored* system (K > 1) - called a spontaneous reaction

Most product-favored reactions are exothermic (ΔH)… but not all.

Nonspontaneous reactions require energy input to occur.

All reactions require activation energy (E_a) to take place

Spontaneity does not imply anything about time for the reaction to occur (i.e. *kinetics*). Spontaneity can be for fast and slow reactions!

The first law of thermodynamics does not predict if a reaction is spontaneous; the first law applies to all systems!

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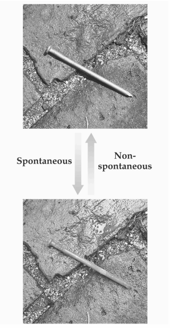
Spontaneous Processes



Processes that are *spontaneous* in one direction are *nonspontaneous* in the reverse direction.

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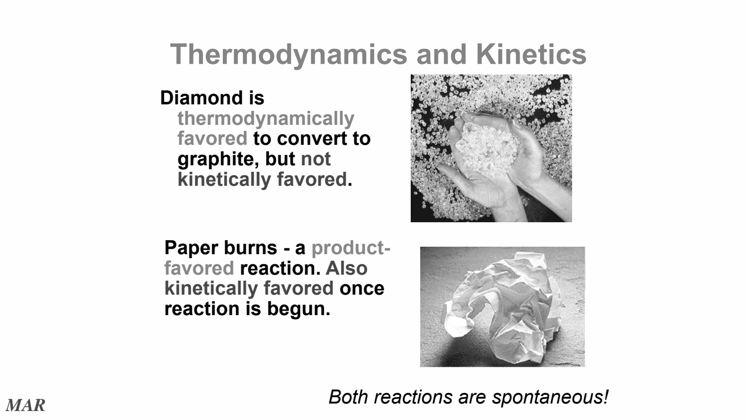

Thermodynamics and Kinetics

Diamond is thermodynamically favored to convert to graphite, but not kinetically favored.

Paper burns - a product-favored reaction. Also kinetically favored once reaction is begun.

Both reactions are spontaneous!

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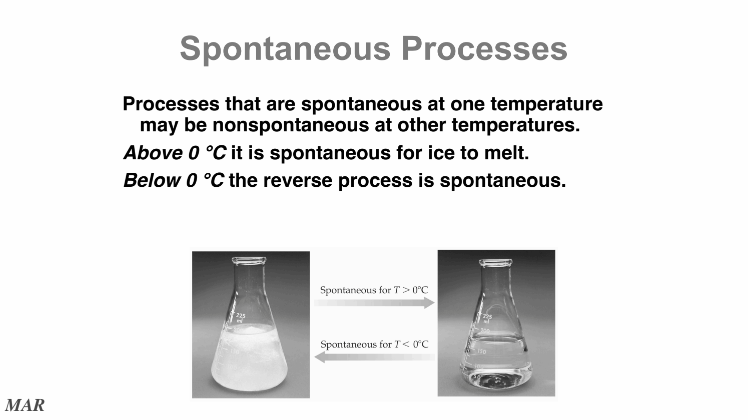

Spontaneous Processes

Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.

Above 0 °C **it is spontaneous for ice to melt.**

Below 0 °C **the reverse process is spontaneous.**

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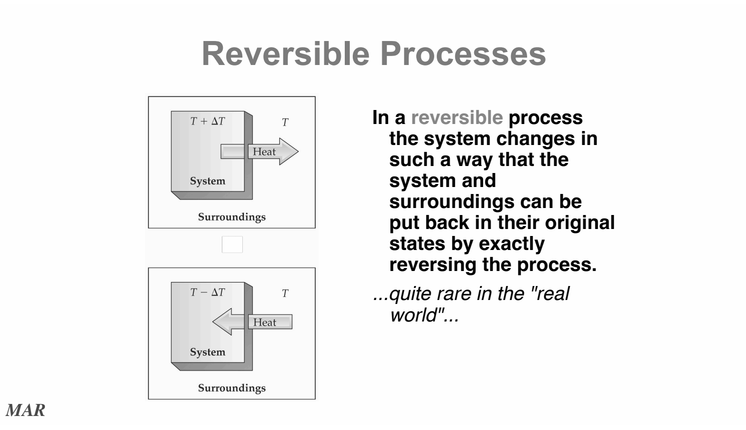
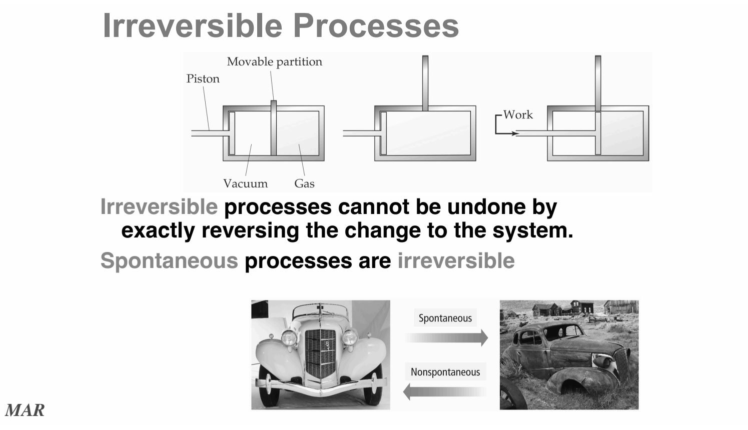


Reversible Processes

In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

...quite rare in the "real world"...

MAR



Irreversible Processes

Irreversible processes cannot be undone by exactly reversing the change to the system.

Spontaneous processes are irreversible

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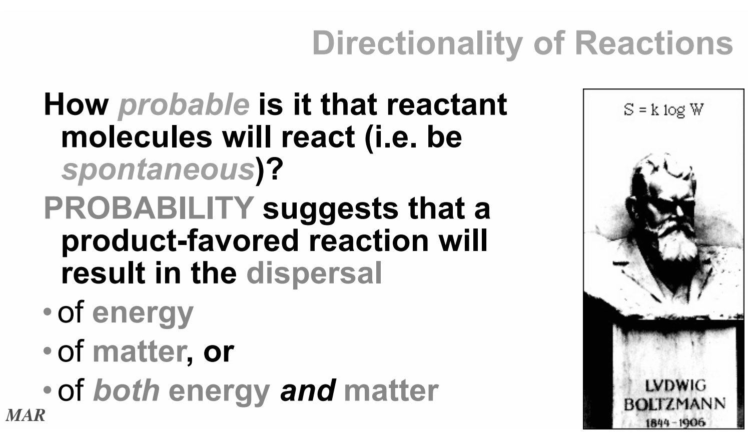

Directionality of Reactions

How *probable* is it that reactant molecules will react (i.e. be *spontaneous*)?

PROBABILITY suggests that a product-favored reaction will result in the dispersal

- of energy
- of matter, **or**
- of *both* energy ***and*** matter

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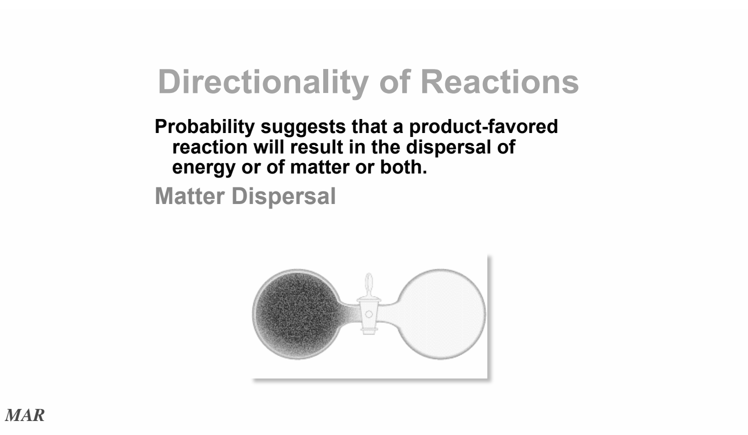
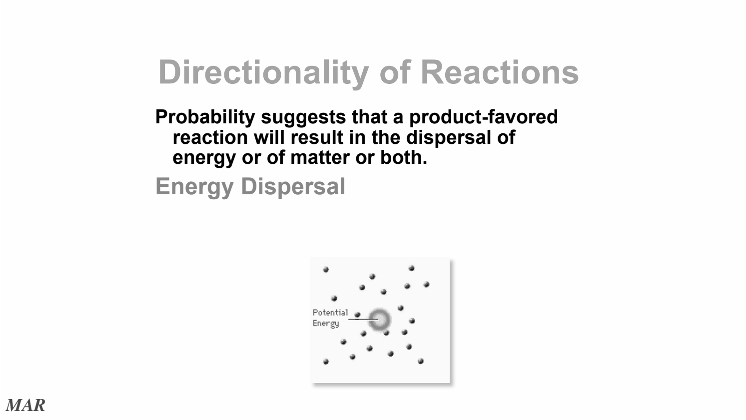


Directionality of Reactions

Probability suggests that a product-favored reaction will result in the dispersal of energy or of matter or both.

Matter Dispersal

MAR



Directionality of Reactions

Probability suggests that a product-favored reaction will result in the dispersal of energy or of matter or both.

Energy Dispersal

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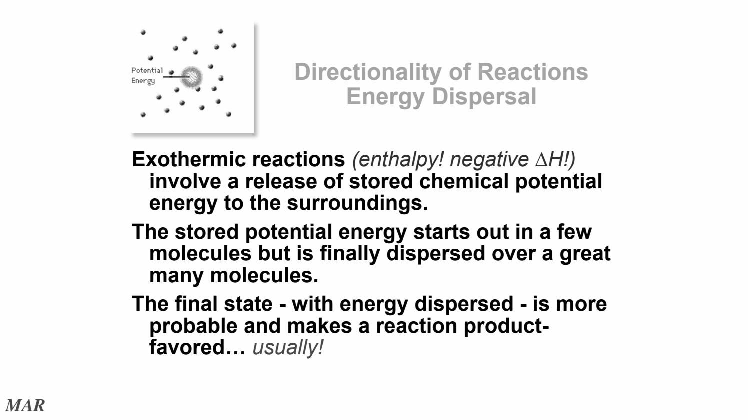

Directionality of Reactions
Energy Dispersal

Exothermic reactions *(enthalpy! negative ΔH!)* **involve a release of stored chemical potential energy to the surroundings.**

The stored potential energy starts out in a few molecules but is finally dispersed over a great many molecules.

The final state - with energy dispersed - is more probable and makes a reaction product-favored… *usually!*

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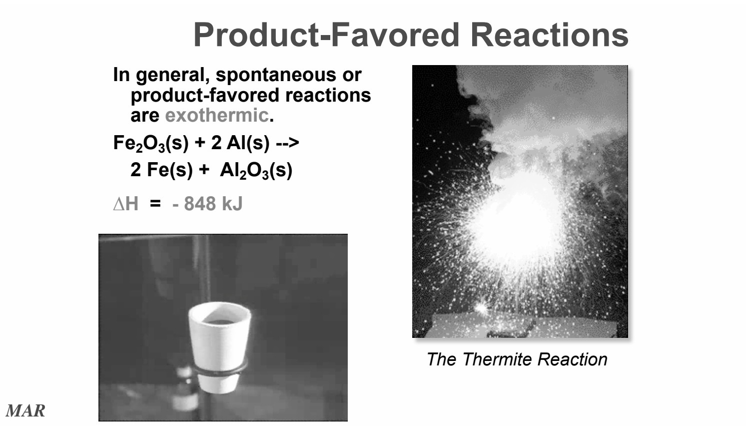

Product-Favored Reactions

In general, spontaneous or product-favored reactions are exothermic.

$Fe_2O_3(s) + 2\ Al(s) \dashrightarrow$
$2\ Fe(s) + Al_2O_3(s)$

$\Delta H = -848$ kJ

The Thermite Reaction

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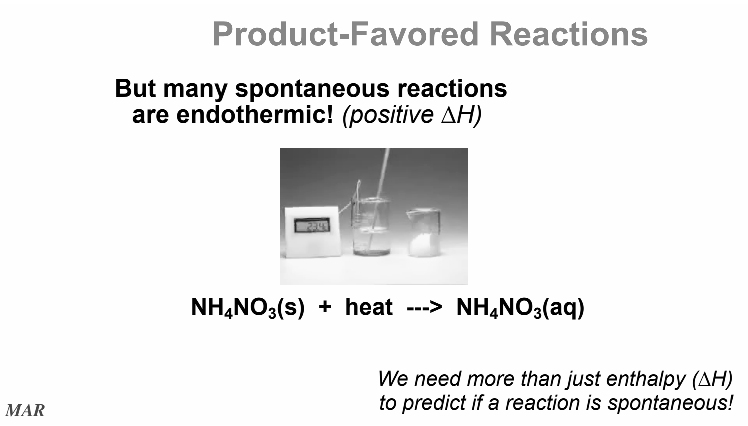

Product-Favored Reactions

But many spontaneous reactions are endothermic! *(positive ΔH)*

$NH_4NO_3(s) + \text{heat} \dashrightarrow NH_4NO_3(aq)$

We need more than just enthalpy (ΔH) to predict if a reaction is spontaneous!

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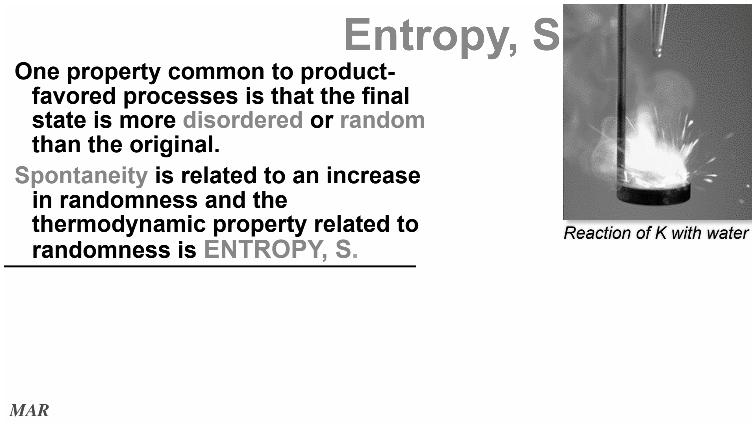


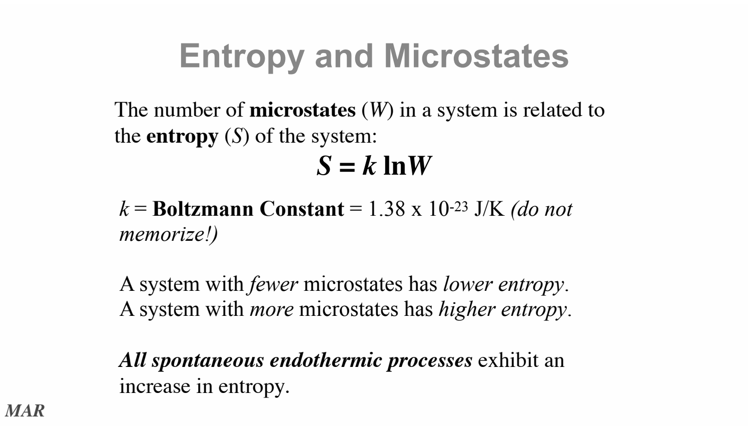
Entropy, S

One property common to product-favored processes is that the final state is more disordered or random than the original.

Spontaneity is related to an increase in randomness and the thermodynamic property related to randomness is ENTROPY, S.

Reaction of K with water

MAR



Entropy and Microstates

The number of **microstates** (*W*) in a system is related to the **entropy** (*S*) of the system:

$$S = k \ln W$$

k = **Boltzmann Constant** = 1.38 x 10^{-23} J/K *(do not memorize!)*

A system with *fewer* microstates has *lower entropy*.
A system with *more* microstates has *higher entropy*.

All spontaneous endothermic processes exhibit an increase in entropy.

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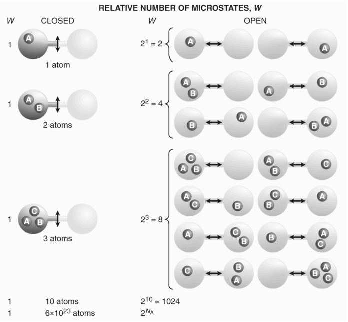
Entropy and Microstates

$S = k \ln W$

When the stopcock opens, the number of microstates is 2^n, where n is the number of particles.

Punchline: the more atoms, the more entropy



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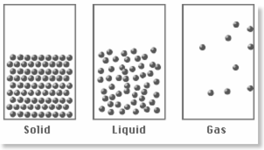
Entropy, S

More disordered substances have higher entropy, *so:*

S (solids) < S (liquids) < S (gases)



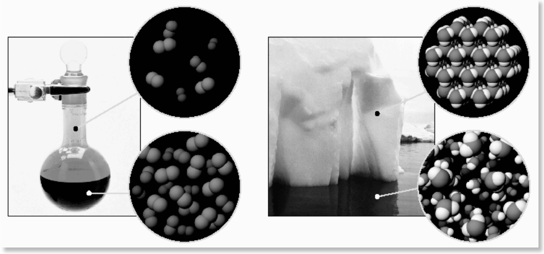
	S^o (J/K•mol)
H_2O(sol)	**47.91**
H_2O(liq)	**69.91**
H_2O(gas)	**188.8**

Only pure (element), perfectly formed crystals at 0 K have zero entropy (S = k ln W where W = 1: the 3rd Law of Thermodynamics)

See the Entropy Guide

MAR

Entropy and States of Matter



S˚(Br_2 liq) < S˚(Br_2 gas) **S˚(H_2O sol) < S˚(H_2O liq)**

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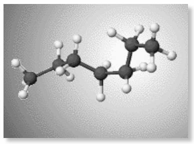
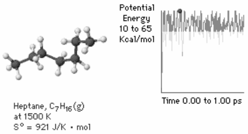
Entropy, S

Entropy of a substance increases with temperature.



Molecular motions of heptane, C_7H_{16}



Molecular motions of heptane at different temps. ***S(1500 K) > S(200 K)***

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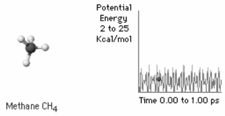
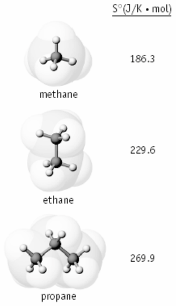


Increases in molecular complexity and molar mass generally lead to increases in S.

	S° (J/mol·K)
He(*g*)	126.2
Ne(*g*)	146.1
Ar(*g*)	154.8
Kr(*g*)	163.8
Xe(*g*)	169.4

Entropy, S



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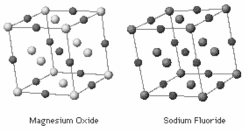
Entropy, S

Entropies of ionic solids depend on coulombic attractions.



Mg^{2+} & O^{2-} **Na^+ & F^-**

	S^o (J/K•mol)
MgO	**26.9**
NaF	**51.5**

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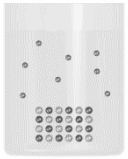
Entropy, S

Entropy usually increases when a pure liquid or solid dissolves in a solvent.



See the Entropy Guide

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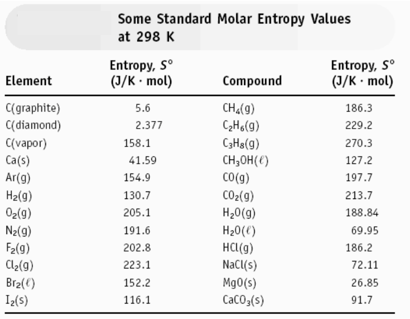
Standard Molar Entropies



Some Standard Molar Entropy Values at 298 K

Element	Entropy, $S°$ (J/K · mol)	Compound	Entropy, $S°$ (J/K · mol)
C(graphite)	5.6	$CH_4(g)$	186.3
C(diamond)	2.377	$C_2H_6(g)$	229.2
C(vapor)	158.1	$C_3H_8(g)$	270.3
Ca(s)	41.59	$CH_3OH(\ell)$	127.2
Ar(g)	154.9	CO(g)	197.7
$H_2(g)$	130.7	$CO_2(g)$	213.7
$O_2(g)$	205.1	$H_2O(g)$	188.84
$N_2(g)$	191.6	$H_2O(\ell)$	69.95
$F_2(g)$	202.8	HCl(g)	186.2
$Cl_2(g)$	223.1	NaCl(s)	72.11
$Br_2(\ell)$	152.2	MgO(s)	26.85
$I_2(s)$	116.1	$CaCO_3(s)$	91.7

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CH 221 / CH 222 "Enthalpy Flashback"

For a temperature change in the same phase (s, l, g) enthalpy (ΔH) equals the heat transferred (q) at constant pressure via:

$$\Delta H = q = mC\Delta T$$

m = mass (g), C = heat capacity (4.184 J g^{-1} K^{-1} for water!), ΔT = final temperature - initial temperature

For a phase change, the enthalpy change:

$$\Delta H = (\text{“mass”})(\text{“heat of something”})$$

*"mass" = grams or moles, "heat of something" depends on phase change, i.e. 333 J/g = heat of **fusion**, 40.7 kJ/mol = heat of **vaporization***

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Entropy Changes for a Temperature Change in the Same Phase

For a temperature change in the same phase,

$$\Delta S = n\,C\,\ln\frac{T_2}{T_1}$$

where
n = moles of substance
C = *molar* heat capacity (at const. P)
T = Kelvin Temperature

For 0.499 mol of H_2O heated from 281 K to 294 K:

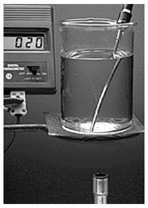
C = 4.184 J g^{-1} K^{-1} * 18.02 g mol^{-1} = 75.40 J mol^{-1} K^{-1}

ΔS = 0.499 mol * 75.40 J mol^{-1} K^{-1} * ln (294/281)

ΔS = 1.70 J K^{-1}

MAR

Entropy Changes for Phase Changes



For a phase change,

$$\Delta S = q/T$$

where q = heat transferred in phase change

For H_2O (liq) ---> $H_2O(g)$,

$\Delta H = q = +40,700$ J/mol

40.7 kJ/mol is ΔH_{vap} for H_2O

$$\Delta S = \frac{q}{T} = \frac{40{,}700\ \text{J/mol}}{373.15\ \text{K}} = +109\ \text{J/K•mol}$$

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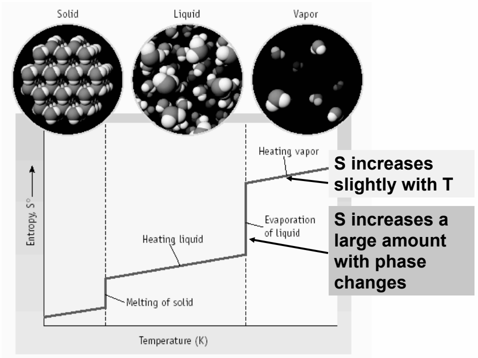
Entropy and Temperature



S increases slightly with T

S increases a large amount with phase changes

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CH 221 / CH 222 "Enthalpy Flashback"

Also: the **system enthalpy** *for a reaction can be calculated:*

$\Delta H_{sys}^o = \Sigma\Delta H^o$ (products) - $\Sigma\Delta H^o$ (reactants)

Find ΔH_{sys}^o ***for:*** $2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(liq)$

$\Delta H^o = 2\ \Delta H^o (H_2O(l)) - [2\ \Delta H^o (H_2) + \Delta H^o (O_2)]$

$\Delta H^o = 2$ mol (-285.85 kJ/mol) - [2 mol (0) + 1 mol (0)]

$\Delta H_{sys}^o = -571.70$ kJ/mol

ΔH for pure elements = 0. Values of ΔH found in tables
This reaction is **exothermic** *due to negative ΔH value (***endothermic*** = positive ΔH). The "°" means "standard conditions" (298 K, 1 atm, 1 M, most common state)*

MAR

Calculating ΔS for a Reaction

$\Delta S_{sys}^o = \Sigma S^o$ **(products) -** ΣS^o **(reactants)**

ΔS_{sys}^o *= "system entropy at standard conditions"*

Calculate ΔS_{sys}^o: $2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(liq)$

Use S° values in tables:

$\Delta S^o = 2\ S^o (H_2O(l)) - [2\ S^o (H_2(g)) + S^o (O_2(g))]$

$\Delta S^o = 2$ mol (69.9 J/K•mol) - [2 mol (130.7 J/K•mol) + 1 mol (205.3 J/K•mol)]

$\Delta S_{sys}^o = -326.9$ J/K

Note that there is a decrease in S because 3 mol of gas give 2 mol of liquid.

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Calculating ΔS_f° for a Reaction

ΔS_f^o *is the "***entropy of formation***" or "***formation entropy***" (which is similar to CH 221's "enthalpy of formation",* ΔH_f^o*); this means:*

- *only one mole of product will be formed*
- *all reactants are elements in their standard states*

Example: **Calculate** ΔS_f^o ***for:*** $H_2(g) + {}^1/_2\ O_2(g) \text{ ---> } H_2O(liq)$

Must use fraction - only 1 mol of product! Use standard element states for reactants. Use S° values in tables:

$\Delta S_f^o = S^o (H_2O(l)) - [S^o (H_2(g)) + {}^1/_2\ S^o (O_2(g))]$

$\Delta S^o =$ 69.9 J/K•mol - [130.7 J/K•mol + ${}^1/_2$ (205.3 J/K•mol)]

$\Delta S_f^o = -163.5$ J/K

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2nd Law of Thermodynamics

A reaction is spontaneous (product-favored) if ΔS for the universe is positive.

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

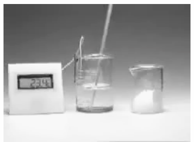
$\Delta S_{universe} > 0$ *(positive)* ***for all product-favored irreversible process***

First calc. entropy created by matter dispersal (ΔS_{system})

Next, calc. entropy created by energy dispersal ($\Delta S_{surround}$)

MAR

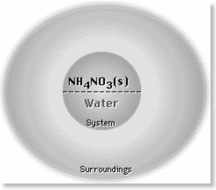
2nd Law of Thermodynamics



Dissolving NH_4NO_3 in water - an entropy driven process:

$NH_4NO_3(s) \rightarrow NH_4NO_3(aq)$

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$



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2nd Law of Thermodynamics

Calculate $\Delta S^o_{universe}$ *for:* **$2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(liq)$**

ΔS^o_{system} **= -326.9 J/K** *(earlier example for ΔS)*

$$\Delta S^o_{surroundings} = \frac{q_{surroundings}}{T} = \frac{-\Delta H_{system}}{T}$$

Can calculate that $\Delta H^o_{system} = -571.70$ kJ

via $\Delta H^o(system) = \Sigma\Delta H^o(prod) - \Sigma\Delta H^o(react)$
$\Delta H^o(system) = 2*\Delta H^o(H_2O) - (2*\Delta H^o(H_2) + \Delta H^o(O_2))$

$$\Delta S^o_{surroundings} = \frac{-(-571.70 \text{ kJ})(1000 \text{ J/kJ})}{298.15 \text{ K}}$$

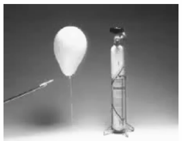
$\Delta S^o_{surroundings}$ **= +1917.5 J/K**

MAR

2nd Law of Thermodynamics

Calculate $\Delta S^o_{universe}$ for:

$2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(liq)$

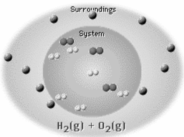


ΔS^o_{system} = -326.9 J/K

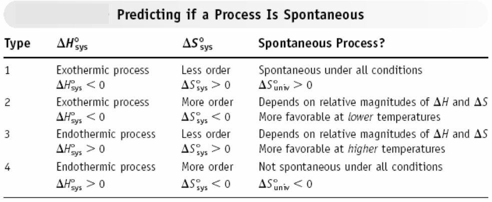
$\Delta S^o_{surroundings}$ = +1917.5 J/K

$\Delta S^o_{universe} = \Delta S^o_{system} + \Delta S^o_{surroundings}$

$\Delta S^o_{universe}$ = *-326.9 + 1917.5 =* +1590.6 J/K



The entropy of the universe is increasing, so the reaction is product-favored.



Predicting if a Process Is Spontaneous

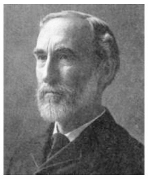
Type	ΔH^o_{sys}	ΔS^o_{sys}	Spontaneous Process?
1	Exothermic process $\Delta H^o_{sys} < 0$	Less order $\Delta S^o_{sys} > 0$	Spontaneous under all conditions $\Delta S^o_{univ} > 0$
2	Exothermic process $\Delta H^o_{sys} < 0$	More order $\Delta S^o_{sys} < 0$	Depends on relative magnitudes of ΔH and ΔS More favorable at *lower* temperatures
3	Endothermic process $\Delta H^o_{sys} > 0$	Less order $\Delta S^o_{sys} > 0$	Depends on relative magnitudes of ΔH and ΔS More favorable at *higher* temperatures
4	Endothermic process $\Delta H^o_{sys} > 0$	More order $\Delta S^o_{sys} < 0$	Not spontaneous under all conditions $\Delta S^o_{univ} < 0$

Spontaneous or Not?

Remember that $-\Delta H^\circ_{sys}$ is proportional to ΔS°_{surr}

An exothermic process has $\Delta S^\circ_{surr} > 0$.

Gibbs Free Energy, G



Josiah Willard Gibbs

$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$

$$\Delta S_{univ} = \frac{-\Delta H_{sys}}{T} + \Delta S_{sys}$$

Multiply through by -T

$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$

$-T\Delta S_{univ}$ = **change in Gibbs free energy for the system =** ΔG_{system}

Under standard conditions -

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

See the Gibbs Free Energy Guide

$\Delta G^o = \Delta H^o - T\Delta S^o$

Gibbs free energy **change =**

total energy change for system

- energy lost in disordering the system

If reaction is

- exothermic (negative ΔH^o) **(energy dispersed)**
- ***and*** entropy increases (positive ΔS^o) **(matter dispersed)**

then ΔG^o **must be** NEGATIVE

Reaction is spontaneous (and product-favored).

$\Delta G^o = \Delta H^o - T\Delta S^o$

Gibbs free energy **change =**

total energy change for system

- energy lost in disordering the system

If reaction is

- **endothermic (positive ΔH^o)**
- ***and* entropy decreases (negative ΔS^o)**

then ΔG^o **must be** POSITIVE

Reaction is not spontaneous (and is reactant-favored).

Gibbs Free Energy, G

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

ΔH^o	ΔS^o	ΔG^o	Reaction
exo(-)	**increase(+)**	**-**	**Prod-favored**
endo(+)	decrease(-)	+	React-favored
exo(-)	**decrease(-)**	**?**	**T dependent**
endo(+)	**increase(+)**	**?**	**T dependent**

spontaneous *means product favored and implies a negative* ΔG

non-spontaneous *means reactant favored and implies a positive* ΔG

Gibbs Free Energy, G

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Two methods for calculating ΔG^o

a) **Determine ΔH^o_{rxn} and ΔS^o_{rxn} and use Gibbs equation.**

b) **Use tabulated values of free energies of formation, ΔG_f^o.**

$$\Delta G^o_{rxn} = \Sigma\ \Delta G_f^o\ (\text{products}) - \Sigma\ \Delta G_f^o\ (\text{reactants})$$

See the Gibbs Free Energy Guide

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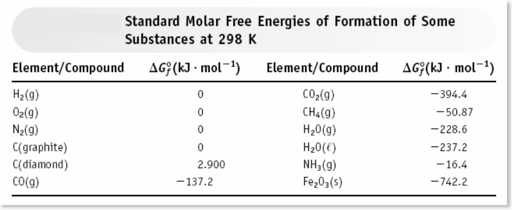
Free Energies of Formation

$$\Delta G^o_{rxn} = \Sigma\ \Delta G_f^o\ (\text{products}) - \Sigma\ \Delta G_f^o\ (\text{reactants})$$



Standard Molar Free Energies of Formation of Some Substances at 298 K

Element/Compound	$\Delta G_f^o (kJ \cdot mol^{-1})$	Element/Compound	$\Delta G_f^o (kJ \cdot mol^{-1})$
$H_2(g)$	0	$CO_2(g)$	−394.4
$O_2(g)$	0	$CH_4(g)$	−50.87
$N_2(g)$	0	$H_2O(g)$	−228.6
C(graphite)	0	$H_2O(\ell)$	−237.2
C(diamond)	2.900	$NH_3(g)$	−16.4
CO(g)	−137.2	$Fe_2O_3(s)$	−742.2

Note that ΔG°_f for an element = 0

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Calculating ΔG^o_{rxn}

$$\Delta G^o_{rxn} = \Sigma\ \Delta G_f^o\ (\text{products}) - \Sigma\ \Delta G_f^o\ (\text{reactants})$$

Combustion of carbon

$C(graphite) + O_2(g) \rightarrow CO_2(g)$

$\Delta G^o_{rxn} = \Delta G_f^o(CO_2) - [\Delta G_f^o(graph) + \Delta G_f^o(O_2)]$

$\Delta G^o_{rxn} = -394.4\ kJ - [0 + 0]$

$\Delta G^o_{rxn} = -394.4\ kJ$

Note that free energy of formation of an element in its standard state is 0.

Reaction is product-favored as expected - *green house gases!*

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Calculating ΔG^o_{rxn}

Some reactions occur spontaneously due to favorable ΔH^o_{rxn} and ΔS^o_{rxn} values.

These reactions are both "enthalpy driven" and "entropy driven"

But not all reactions have favorable enthalpy and entropy values…

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Calculating ΔG^o_{rxn}

Example: *Find ΔG^o_{rxn} for the combustion of acetylene:*

$C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(g)$

*** Use enthalpies of formation to calculate**
$\Delta H^o_{rxn} = -1238\ kJ$ *$\Delta H^o(rxn) = \Sigma\Delta H^o(prod) - \Sigma\Delta H^o(react)$*

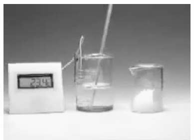
*** Use standard molar entropies to calculate**
$\Delta S^o_{rxn} = -97.4\ J/K$ or $-0.0974\ kJ/K$ *ditto for $\Delta S^o(rxn)$*

*** $\Delta G^o_{rxn} = -1238\ kJ - (298\ K)(-0.0974\ kJ/K)$**
$= -1209\ kJ$

Reaction is product-favored despite negative ΔS^o_{rxn}. Reaction is "enthalpy driven"

MAR

Calculating ΔG^o_{rxn}



$NH_4NO_3(s) + \text{heat} \rightarrow NH_4NO_3(aq)$

Is the dissolution of ammonium nitrate product-favored?

If so, is it enthalpy- or entropy-driven?

MAR

Calculating ΔG^o_{rxn}

Find ΔG^o_{rxn} *:* **$NH_4NO_3(s)$ + heat ---> $NH_4NO_3(aq)$**

From tables of thermodynamic data we find

ΔH^o_{rxn} = +25.7 kJ *$\Delta H^o(rxn) = \Sigma\Delta H^o(prod) - \Sigma\Delta H^o(react)$*

ΔS^o_{rxn} = +108.7 J/K *or* **+0.1087 kJ/K** *ditto for $\Delta S^o(rxn)$*

ΔG^o_{rxn} = +25.7 kJ - (298 K)(+0.1087 kJ/K)

= -6.7 kJ

Reaction is product-favored in spite of positive ΔH^o_{rxn}.

Reaction is "entropy driven"

MAR

Free Energy and Threshold Temperature

$2\ Fe_2O_3(s) + 3\ C(s) \text{ ---> } 4\ Fe(s) + 3\ CO_2(g)$

ΔH^o_{rxn} = +467.9 kJ ΔS^o_{rxn} = +560.3 J/K

ΔG^o_{rxn} = +300.8 kJ

Reaction is reactant-favored at 298 K

At what Threshold Temperature does ΔG^o_{rxn} just change from being (+) to being (-)?

When $\Delta G^o_{rxn} = 0 = \Delta H^o_{rxn} - T\Delta S^o_{rxn}$

$$T = \frac{\Delta H_{rxn}}{\Delta S_{rxn}} = \frac{467.9 \text{ kJ}}{0.5603 \text{ kJ/K}} = 835.1 \text{ K}$$

***If* ΔH *and* ΔS have the same sign**, calculating the *Threshold Temperature* (between spontaneous and nonspontaneous reactions) can be important!

MAR

Free Energy and Temperature

Another example:

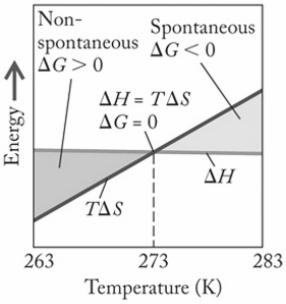
$H_2O(s) \rightarrow H_2O(l)$ at 273 K

ΔH = *positive*

ΔS = *positive*

$\Delta G = \Delta H - T\Delta S$

= negative above a certain temperature, when $T\Delta S > \Delta H$



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Free Energy and Equilibrium

K_{eq} is related to reaction favorability and ΔG^o_{rxn}

The more negative the value of ΔG^o_{rxn} the larger the value of K.

$$\Delta G^o_{rxn} = - RT \ln K$$

where R = 8.3145 J/K•mol

If not at standard states (i.e **ΔG_{rxn}***) then:*

$\Delta G_{rxn} = \Delta G^o_{rxn} + RT \ln Q$

Find ΔG^o_{rxn} with K first, then solve for ΔG_{rxn}

See the <u>Gibbs Free Energy Guide</u>

MAR

Thermodynamics and K_{eq}

$$\Delta G^o_{rxn} = - RT \ln K$$

Calculate K for the reaction:

$N_2O_4 \text{ ---> } 2\ NO_2$ **ΔG^o_{rxn} = +4.80 kJ**

ΔG^o_{rxn} = +4800 J = - (8.3145 J/K)(298 K) ln K

$$\ln K = -\frac{4800 \text{ J}}{(8.3145 \text{ J/K})(298\text{K})} = -1.94$$

K = $e^{-1.94}$ = 0.14

***When* ΔG^o_{rxn} > 0, *then* K < 1**

***and when* ΔG^o_{rxn} < 0, *then* K > 1**

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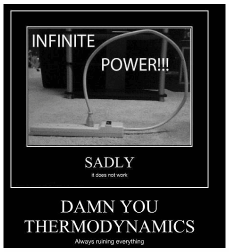

See:

- *<u>Chapter Sixteen Study Guide</u>*
- *<u>Chapter Sixteen Concept Guide</u>*
- *<u>Types of Equilibrium Constants</u>*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*

End of Chapter 16

The bankruptcy sale at the Entropy Institute was going to more difficult than Dave thought it'd be.

MAR

Important Equations, Constants, and Handouts from this Chapter:

$\Delta H_{sys}^{o} = \Sigma\Delta H^{o}$ **(products) -** $\Sigma\Delta H^{o}$ **(reactants)**

$\Delta S_{sys}^{o} = \Sigma S^{o}$ **(products) -** ΣS^{o} **(reactants)**

$\Delta G_{sys}^{o} = \Sigma\Delta G^{o}$ **(products) -** $\Sigma\Delta G^{o}$ **(reactants)**

$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$

$\Delta G^{o}_{rxn} = -RT \ln K$

$R = 8.3145\ J\ mol^{-1}\ K^{-1}$

$\Delta G_{rxn} = \Delta G^{o}_{rxn} + RT \ln Q$

Handouts:

- *Types of Equilibrium Constants*
- *Thermodynamic Values (Problem Set #5)*

- *know the* **three laws** *of* **thermodynamics!**
- *know the* **difference between enthalpy and entropy** *and* **how they relate to Gibbs free energy**
- *know how to* **calculate enthalpy (CH 221) entropy and Gibbs energy (this chapter)**
- *know how the* **sign of** ΔG **relates to spontaneity (and also** $\Delta S_{universe}$**)**

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End of Chapter Problems: *Test Yourself*

You will need a table of thermodynamic values found in problem set #5

1. Use $S°$ values to calculate the entropy change, $\Delta S°$, for the following process: $Br_2(l) \rightarrow Br_2(g)$
2. Calculate $\Delta H°$ and $\Delta S°$ for the reaction: $\mathbf{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$ Is the reaction predicted to be spontaneous at room temperature? higher temperatures?
3. Using values of $\Delta G°_f$, calculate $\Delta G°_{rxn}$ for: $\mathbf{2\ K(s) + Cl_2(g) \rightarrow 2\ KCl(s)}$
4. Estimate the temperature required to decompose HgS(s, red) into Hg(l) and S(g).
5. Calculate $\Delta G°$ and K_p at 25 °C for the reaction: $2\ HBr(g) + Cl_2(g) \rightarrow 2\ HCl(g) + Br_2(l)$ Is the reaction predicted to be product-favored under standard conditions?

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End of Chapter Problems: *Answers*

1. 93.3 J/K
2. $\Delta H° = 191.59$ kJ, $\Delta S° = 141.9$ J/K, $\Delta G° = 149.3$ kJ (298 K), not spontaneous, but reaction should be spontaneous at higher temperatures (entropy driven)
3. $\Delta G°_{rxn} = -817.0$ kJ, spontaneous
4. T = 2089 K and greater
5. $\Delta G° = -83.74$ kJ, and $K_p = 4.8 \times 10^{14}$ *product favored*

You will need a table of thermodynamic values found in problem set #5

MAR

ELECTROCHEMISTRY

Chapter 17

Chemistry 223

Professor Michael Russell

Last update: 4/29/24

TRANSFER REACTIONS

Atom / Group transfer

$HOAc(aq) + H_2O(l) \rightarrow OAc^{-1}(aq) + H_3O^+(aq)$

Electron transfer

$Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$

TRANSFER REACTIONS

Electron Transfer Reactions:

$$Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$$

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$$

and

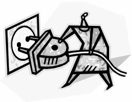
$$2\,Ag^+(aq) + 2\,e^- \rightarrow 2\,Ag(s)$$

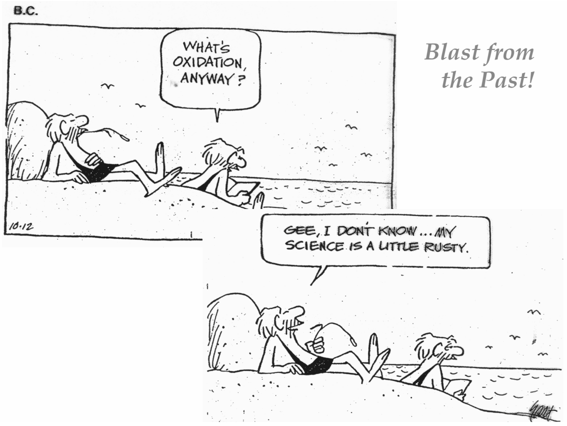
Electron Transfer Reactions

Electron transfer reactions are oxidation-reduction or redox reactions.

Redox reactions can result in the generation of an electric current or be caused by imposing an electric current.

Therefore, this field of chemistry is often called ELECTROCHEMISTRY.





Blast from the Past!

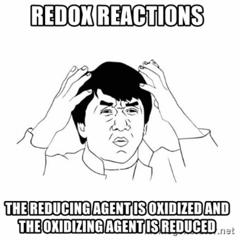
OXIDATION - loss of electron(s) by a species; increase in oxidation number.

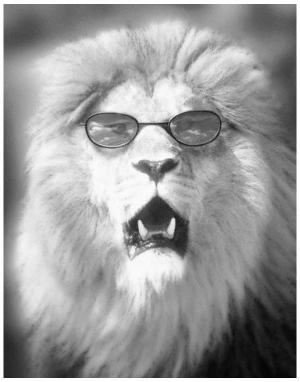
REDUCTION - gain of electron(s); decrease in oxidation number.

OXIDIZING AGENT - electron acceptor; species is reduced.

REDUCING AGENT - electron donor; species is oxidized.

Review of Terminology for Redox Reactions





LEO
says
GER

MAR

LEO **says** GER

Lose	Gain
Electrons	Electrons
Oxidized	Reduced

$\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e-}$ ***Oxidized***

$\text{Cu}^{2+} + 2\text{e-} \rightarrow \text{Cu(s)}$ ***Reduced***

Can also use ***"OIL RIG":***
OIL = "Oxidation is Losing" *(electrons)*
RIG = "Reduction is Gaining" *(electrons)*

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OXIDATION-REDUCTION REACTIONS

Direct Redox Reaction

Oxidizing and reducing agents in direct contact.

$\text{Cu(s)} + 2\,\text{Ag}^{+}\text{(aq)} \rightarrow \text{Cu}^{2+}\text{(aq)} + 2\,\text{Ag(s)}$

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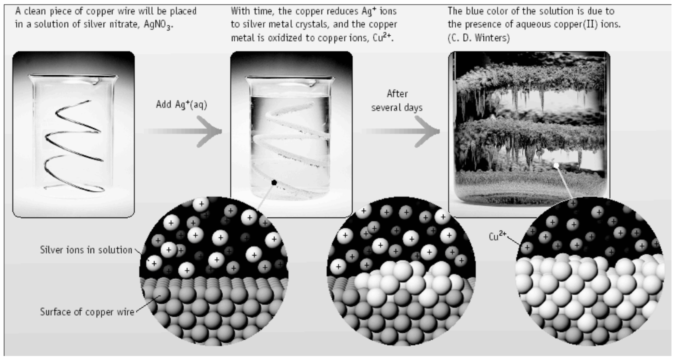
Copper + Silver Ion



A clean piece of copper wire will be placed in a solution of silver nitrate, $AgNO_3$.

With time, the copper reduces Ag^+ ions to silver metal crystals, and the copper metal is oxidized to copper ions, Cu^{2+}.

The blue color of the solution is due to the presence of aqueous copper(II) ions. (C. D. Winters)

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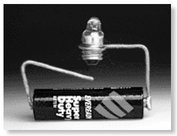
OXIDATION-REDUCTION REACTIONS

Indirect Redox Reaction

A battery functions by transferring electrons through an external wire from the reducing agent to the oxidizing agent.



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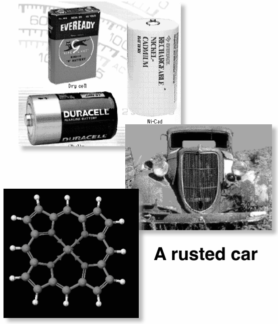
Why Study Electrochemistry?

- **Batteries**
- **Corrosion**
- **Industrial production of chemicals such as Cl_2, NaOH, F_2 and Al**
- **Biological redox reactions**



A rusted car

The heme group

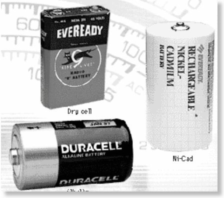
MAR

Electrochemical Cells

An apparatus that allows a redox reaction to occur by transferring electrons through an external connector.

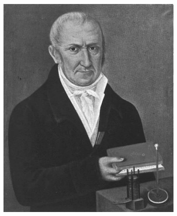
Product favored reaction ---> voltaic or galvanic cell ----> electric current created

Reactant favored reaction ---> electrolytic cell ---> electric current used to cause chemical change



Batteries are voltaic cells

Famous Electrochemists



Alessandro Volta, 1745-1827, Italian scientist and inventor.

Luigi Galvani, 1737-1798, Italian scientist and inventor.

Balancing Equations for Redox Reactions

Some redox reactions have equations that must be balanced by special techniques.

$MnO_4^- + 5 Fe^{2+} + 8 H^+ \rightarrow Mn^{2+} + 5 Fe^{3+} + 4 H_2O$

Mn = +7 Fe = +2 Mn = +2 Fe = +3

See: Redox Reactions Handout

Balancing Equations

Consider the reduction of Ag^+ ions with copper metal.

$Cu + Ag^+$ --gives--> $Cu^{2+} + Ag$

Balancing Equations

Step 1: **Divide the reaction into half-reactions, one for oxidation and the other for reduction.**

Ox $Cu \rightarrow Cu^{2+}$

Red $Ag^+ \rightarrow Ag$

Step 2: **Balance each for mass. Already done in this case.**

Step 3: **Balance each half-reaction for charge by adding electrons.**

Ox $Cu \rightarrow Cu^{2+} + 2e^-$

Red $Ag^+ + e^- \rightarrow Ag$

Balancing Equations

Step 4: **Multiply each half-reaction by a factor that means the reducing agent supplies as many electrons as the oxidizing agent requires.**

Reducing agent Cu $\rightarrow$ Cu^{2+} + 2e-

Oxidizing agent 2 Ag^+ + 2 e- $\rightarrow$ 2 Ag

Step 5: **Add half-reactions to give the overall equation.**

$$\boxed{Cu + 2 Ag^+ \rightarrow Cu^{2+} + 2 Ag}$$

The equation is now balanced for both charge and mass.

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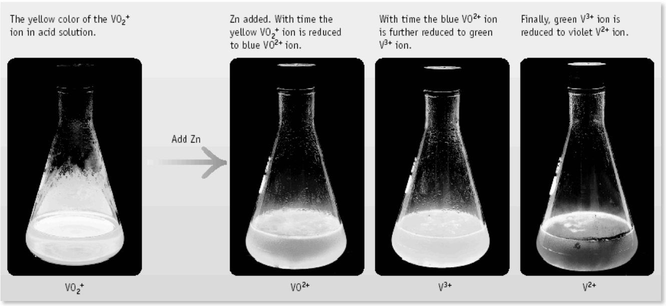
Reduction of VO_2^+ with Zn


The yellow color of the VO_2^+ ion in acid solution.

Zn added. With time the yellow VO_2^+ ion is reduced to blue VO^{2+} ion.

With time the blue VO^{2+} ion is further reduced to green V^{3+} ion.

Finally, green V^{3+} ion is reduced to violet V^{2+} ion.

MAR

Balancing Equations

Balance the following in *acidic* solution-

VO_2^+ + Zn $\rightarrow$ VO^{2+} + Zn^{2+}

Step 1: **Write the half-reactions**

Ox Zn $\rightarrow$ Zn^{2+}

Red VO_2^+ $\rightarrow$ VO^{2+} *(V^{5+} → V^{4+})*

Step 2: **Balance each half-reaction for mass.**

Ox Zn $\rightarrow$ Zn^{2+}

Red VO_2^+ $\rightarrow$ VO^{2+} + H_2O

MAR

Balancing Equations

Balance the following in *acidic* solution-

VO_2^+ + Zn $\rightarrow$ VO^{2+} + Zn^{2+}

Step 1: **Write the half-reactions**

Ox Zn $\rightarrow$ Zn^{2+}

Red VO_2^+ $\rightarrow$ VO^{2+} *(V^{5+} --> V^{4+})*

Step 2: **Balance each half-reaction for mass.**

Ox Zn $\rightarrow$ Zn^{2+}

Red 2 H^+ + VO_2^+ $\rightarrow$ VO^{2+} + H_2O

Add H_2O on O-deficient side and add H^+ on other side for balancing hydrogen

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Balancing Equations

Step 3: **Balance half-reactions for charge.**

Ox Zn $\rightarrow$ Zn^{2+} + 2e-

Red e- + 2 H^+ + VO_2^+ $\rightarrow$ VO^{2+} + H_2O

Step 4: **Multiply by an appropriate factor.**

Ox Zn $\rightarrow$ Zn^{2+} + 2e-

Red 2 e- + 4 H^+ + 2 VO_2^+
$\rightarrow$ 2 VO^{2+} + 2 H_2O

Step 5: **Add half-reactions**

$$\boxed{Zn + 4 H^+ + 2 VO_2^+ \rightarrow Zn^{2+} + 2 VO^{2+} + 2 H_2O}$$

MAR

Balancing Equations

Balance the following in *basic* solution-

MnO_4^{1-} + HO_2^- $\rightarrow$ MnO_4^{2-} + O_2

Step 1: **Write the half-reactions**

Ox HO_2^- $\rightarrow$ O_2 *(peroxide: O^{-1} → O^0)*

Red MnO_4^{1-} $\rightarrow$ MnO_4^{2-} *(Mn^{7+} → Mn^{6+})*

Step 2: **Balance each half-reaction for mass.**

Red MnO_4^{1-} $\rightarrow$ MnO_4^{2-}

Ox HO_2^- $\rightarrow$ O_2 + H_2O

MnO_4^{-1} = permanganate
MnO_4^{2-} = manganate

MAR

Balancing Equations

Balance the following in *basic* solution-

$MnO_4^{1-} + HO_2^- \rightarrow MnO_4^{2-} + O_2$

Step 1: **Write the half-reactions**

Ox $HO_2^- \rightarrow O_2$ *(peroxide: $O^{-1} \rightarrow O^0$)*

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$ *($Mn^{7+} \rightarrow Mn^{6+}$)*

Step 2: **Balance each half-reaction for mass.**

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$

Ox $OH^- + HO_2^- \rightarrow O_2 + H_2O$

Add H_2O on H-deficient side and add OH^- on other side for balancing oxygen

MAR

Balancing Equations

Step 3: **Balance half-reactions for charge.**

Ox $OH^- + HO_2^- \rightarrow O_2 + H_2O + 2e-$

Red $e- + MnO_4^{1-} \rightarrow MnO_4^{2-}$

Step 4: **Multiply by an appropriate factor.**

Ox $OH^- + HO_2^- \rightarrow O_2 + H_2O + 2e-$

Red $2\,e- + 2\,MnO_4^{1-} \rightarrow 2\,MnO_4^{2-}$

Step 5: **Add half-reactions**

$$\boxed{OH^- + HO_2^- + 2\,MnO_4^{1-} \rightarrow O_2 + H_2O + 2\,MnO_4^{2-}}$$

*Add H_2O on H-deficient side and add OH^- on other side for balancing oxygen **in basic solution***

MAR

Alternate Basic Balancing Method

Balance basic reactions first with acid, then "neutralize" with OH^-. *Previous example:*

$MnO_4^{1-} + HO_2^- \rightarrow MnO_4^{2-} + O_2$

Step 1: **Write the half-reactions**

Ox $HO_2^- \rightarrow O_2$

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$

Step 2: **Balance each half-reaction for mass - use H^+ and/or H_2O.**

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$

Ox $HO_2^- \rightarrow O_2 + H^+$

Add H^+ to H-deficient side and H_2O to balance oxygen

MAR

Alternate Basic Balancing Method

Step 3: **Balance half-reactions for charge.**

Ox $HO_2^- \rightarrow O_2 + H^+ + 2e-$

Red $e- + MnO_4^{1-} \rightarrow MnO_4^{2-}$

Step 4: **Multiply by an appropriate factor.**

Ox $HO_2^- \rightarrow O_2 + H^+ + 2e-$

Red $2\,e- + 2\,MnO_4^{1-} \rightarrow 2\,MnO_4^{2-}$

Step 5: **Add half-reactions**

$HO_2^- + 2\,MnO_4^{1-} \rightarrow O_2 + H^+ + 2\,MnO_4^{2-}$

This equation is balanced for pH < 7 but not base

MAR

Alternate Basic Balancing Method

Step 6: **Neutralize H^+ by adding OH^-.**

H^+ and OH^- make H_2O.

Add OH^- to *both* sides of equation

$$HO_2^- + 2\,MnO_4^{1-} + OH^- \rightarrow O_2 + \boxed{H^+ + OH^-} + 2\,MnO_4^{2-}$$

$$\boxed{HO_2^- + 2\,MnO_4^{1-} + OH^- \rightarrow O_2 + H_2O + 2\,MnO_4^{2-}}$$

Use either method to balance basic redox reactions

Also see the <u>Redox Reactions Handout</u>

MAR

Tips on Balancing Equations

- **Determine the pH of the reaction.**
- **Never add O_2, O atoms, or O^{2-} to balance oxygen.**
- **Never add H_2 or H atoms to balance hydrogen.**
- **Be sure to write the correct charges on all the ions.**
- **Check your work at the end to make sure mass and charge are balanced.**
- *See: <u>Redox Reactions Handout</u>*

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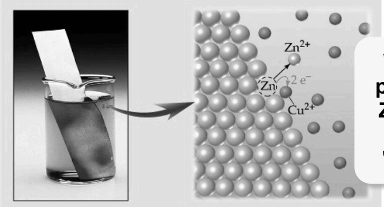
CHEMICAL CHANGE --> ELECTRIC CURRENT



With time, Cu plates out onto Zn metal strip, and Zn strip "disappears."

Zn is oxidized and is the reducing agent

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e-$

Cu^{2+} is reduced and is the oxidizing agent

$Cu^{2+}(aq) + 2e- \longrightarrow Cu(s)$

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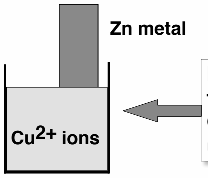
CHEMICAL CHANGE --> ELECTRIC CURRENT



Electrons are transferred from Zn to Cu^{2+}, but there is no useful electric current.

Oxidation: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e-$

Reduction: $Cu^{2+}(aq) + 2e- \longrightarrow Cu(s)$

$Cu^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cu(s)$

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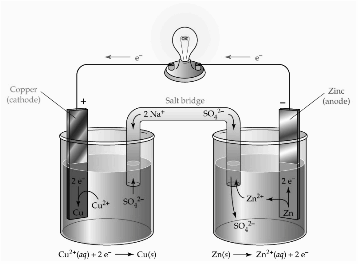
CHEMICAL CHANGE --> ELECTRIC CURRENT

To obtain a useful current, we separate the oxidizing and reducing agents so that electron transfer occurs through an external wire.

This is accomplished in a GALVANIC or VOLTAIC cell.

A group of such cells is called a battery.



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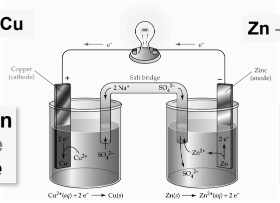
$Cu^{2+} + 2e- \rightarrow Cu$

$Zn \rightarrow Zn^{2+} + 2e-$



Reduction
Cathode
Positive

Oxidation
Anode
Negative

Anions-->
<--Cations

Electrons travel through external wire.
Salt bridge allows anions and cations to move between electrode compartments, maintaining electrical neutrality.

Salt Bridge

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A Red Cat and An Ox

Red Cat = REDuction
at the CAThode
$Cu^{2+} + 2e- \rightarrow Cu$

An Ox = OXidation
at the ANode
$Zn \rightarrow Zn^{2+} + 2e-$

also remember:
oxidation = reducing agent
reduction = oxidizing agent

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SHORTHAND NOTATION for GALVANIC CELLS

$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$
can also be written as:

anode half cell *cathode half cell*

$$\boxed{Zn(s) \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu(s)}$$

phase boundary *salt bridge* *phase boundary*

Electrons flow this way →

oxidation ***reduction***

FAT CAT = *electrons flow* **F***rom* **A***node* **T***o* **CAT***hode*

MAR

SHORTHAND NOTATION for GALVANIC CELLS

Example: Describe the following *galvanic* cell:

$Cu(s)$ | $Cu^{2+}(1.0\ M)$ || $Cl_2(1.0\ atm)$ | $Cl^-(1.0\ M)$ | $Pt(s)$

Solution:

The **anode** (oxidation) is: **$Cu(s) \rightarrow Cu^{2+}_{(aq)} + 2\ e^-$**
and $[Cu^{2+}] = 1.0$ M

The **cathode** (reduction) is: **$Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-_{(aq)}$**
and $[Cl^-] = 1.0$ M and $P(Cl_2) = 1.0$ atm

The cathode uses a **Platinum electrode** to transfer electrons to the $Cl_{2(g)}$. The Pt does not react chemically with the electrons

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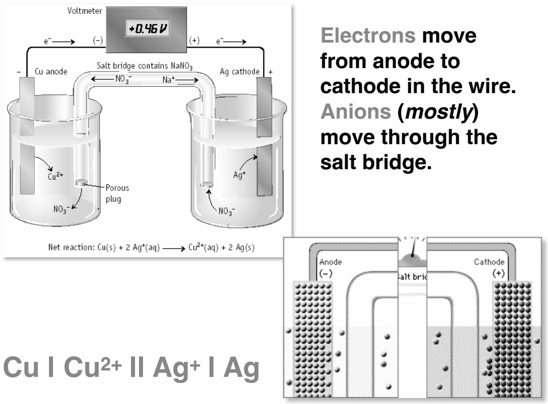
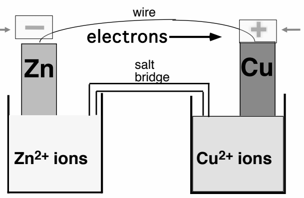


Electrons move from anode to cathode in the wire. Anions (*mostly*) move through the salt bridge.

Cu I Cu^{2+} II Ag^+ I Ag

MAR

Sign of Battery Terminals (Galvanic Cells Only)



Anode, site of *oxidation*, negative

Cathode, site of *reduction*, positive

Electrons flow away from the "negative" terminal (anode) and to the "positive" terminal (cathode) in Galvanic cells

Electrolytic cells use opposite signs

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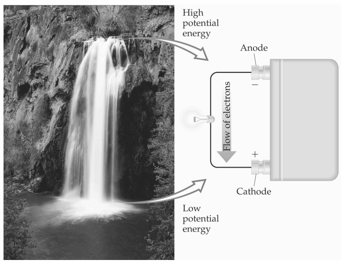
Electromotive Force (emf)

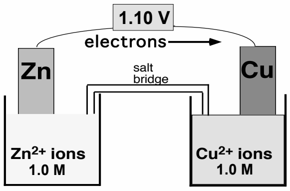


Water only spontaneously flows one way in a waterfall.

Likewise, electrons only spontaneously flow one way in a redox reaction—from higher to lower potential energy.

MAR

CELL POTENTIAL, E

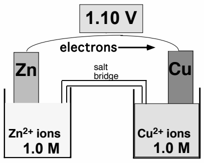


Electrons are "driven" from anode to cathode by an electromotive force or emf.

For Zn/Cu cell, this is indicated by a voltage of 1.10 V at 25 ˚C and when $[Zn^{2+}]$ and $[Cu^{2+}] = 1.0$ M.

Note that 1 V = 1 J/C, more on this later

MAR



CELL POTENTIAL, E

For Zn/Cu cell, voltage is 1.10 V at 25 ˚C and when $[Zn^{2+}]$ and $[Cu^{2+}] = 1.0$ M.

This is the *STANDARD* CELL POTENTIAL, E˚

E˚ *(measured in* Volts, V*)* is a quantitative measure of the tendency for reactants to proceed to products when all are in their standard states at 1.0 M and 25 ˚C.

MAR

Calculating Cell Voltage

Balanced half-reactions can be added together to get overall, balanced equation.

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$

If we know E° for each half-reaction, we can calculate E° for net reaction.

MAR

CELL POTENTIALS, E°

Cannot measure 1/2 reaction E° directly. Therefore, measure it relative to a STANDARD HYDROGEN CELL, SHE.

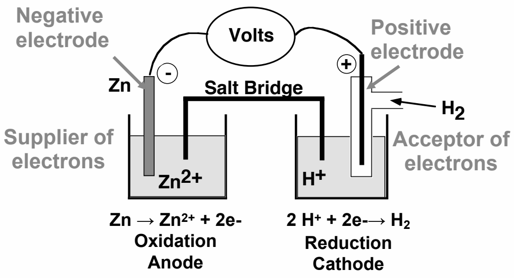
(SHE = Standard Hydrogen Electrode)

$$\boxed{2\,H^+(aq, 1\,M) + 2e^- \rightleftarrows H_2(g, 1\,atm)}$$

$$E^\circ = 0.00\ V$$

MAR

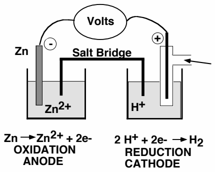
Zn/SHE half cell



E° for the cell =** +0.76 V **(measured)

MAR

Zn/SHE half cell



How to find the zinc half cell potential, E_{Zn}°:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$E_{Zn}^\circ = ?$
$2\,H^+(aq) + 2e^- \rightarrow H_2(g)$	$E_{H+}^\circ = 0.00\ V$
$Zn(s) + 2\,H^+(aq) \rightarrow Zn^{2+} + H_2(g)$	$E_{net}^\circ = +0.76\ V$

so $E_{zn}^\circ = E_{net}^\circ - E_{H+}^\circ = 0.76 - 0.00 = +0.76\ V$

Therefore, E° **for** $Zn \rightarrow Zn^{2+}(aq) + 2e^-$ **is** +0.76 V

Zn is a better **reducing agent than H_2.**

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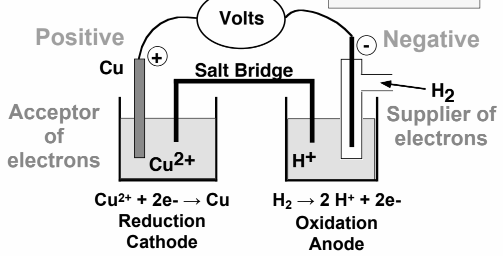
Cu/Cu^{2+} and H_2/H^+ Cell

$\boxed{E^\circ = +0.34\ V}$



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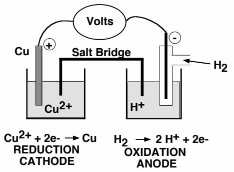
Cu/Cu^{2+} and H_2/H^+ Cell



Overall reaction is reduction of Cu^{2+} by H_2 gas.

$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2\,H^+(aq)$

Measured E° = +0.34 V

Therefore, E° for $Cu^{2+} + 2e^- \rightarrow Cu$ **is**

+0.34 V

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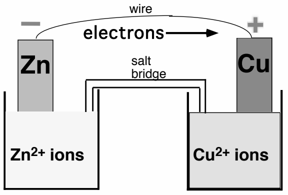
Zn/Cu Electrochemical Cell

Anode, negative, source of electrons



Cathode, positive, sink for electrons

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ Eº = +0.76 V

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ Eº = +0.34 V

$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$

Eº (calc'd) = +1.10 V

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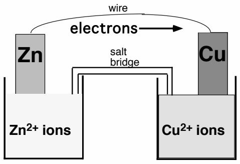
Uses of E° Values

Half-reactions organized by relative ability to act as *oxidizing agents*

Use tables of reduction potentials in your textbook or problem set to predict the direction of redox reactions.



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Reversing Half Reactions

Reversing half reactions **changes the** sign ***but not the magnitude*** **of E˚ values**

Example:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ Eº = +0.76 V

would become

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ Eº = -0.76 V

Because E˚ tables listed as reductions, many negative E˚ values will appear

Negative E˚ values **imply** great oxidizers / reducing agents

Positive E˚ values **imply** great reducers / oxidizing agents

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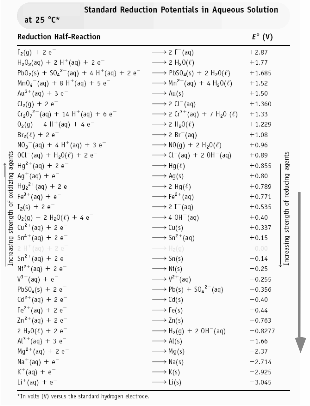
reducing ability increases *or* oxidizing agent capacity increases



Standard Reduction Potentials in Aqueous Solution at 25 °C*

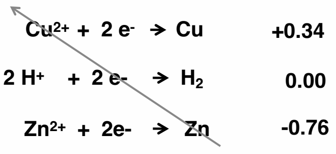
Reduction Half-Reaction		E° (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(\ell)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow PbSO_4(s) + 2H_2O(\ell)$	+1.685
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(\ell)$	+1.52
$Au^{3+}(aq) + 3e^-$	$\longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	+1.360
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(\ell)$	+1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(\ell)$	+1.229
$Br_2(\ell) + 2e^-$	$\longrightarrow 2Br^-(aq)$	+1.08
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow NO(g) + 2H_2O(\ell)$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2e^-$	$\longrightarrow Cl^-(aq) + 2OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2e^-$	$\longrightarrow Hg(\ell)$	+0.855
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	+0.80
$Hg_2^{2+}(aq) + 2e^-$	$\longrightarrow 2Hg(\ell)$	+0.789
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	+0.771
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	+0.535
$O_2(g) + 2H_2O(\ell) + 4e^-$	$\longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	+0.337
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\longrightarrow V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2e^-$	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.763
$2H_2O(\ell) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.714
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.925
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.045

*In volts (V) versus the standard hydrogen electrode.

oxidizing ability increases *or* reducing agent capacity increases

MAR

Standard Redox Potentials, E°



$Cu^{2+} + 2e^- \rightarrow Cu$ +0.34

$2H^+ + 2e^- \rightarrow H_2$ 0.00

$Zn^{2+} + 2e^- \rightarrow Zn$ -0.76

Any substance on the right will reduce any substance higher than it on the left.

Northwest-southeast rule: **product-favored reactions occur between reducing agent at southeast corner (anode) and oxidizing agent at northwest corner (cathode).**

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Calculating Eº (Michael's Method)

Flip one half-reaction from table (and E˚ value), then *add* oxidation and reduction values

Example: **Determine E˚ for the following:**

$2Al + 3Ni^{2+} \rightarrow 2Al^{3+} + 3Ni$

Solution: **From redox tables we find:**

$Al^{3+} + 3e^- \rightarrow Al$ E˚ = -1.66 V

$Ni^{2+} + 2e^- \rightarrow Ni$ E˚ = -0.25 V

Ni^{2+} ok as written; need to flip Al^{3+} reaction to:

$Al \rightarrow Al^{3+} + 3e^-$ E˚ = +1.66 V

So: **E˚ = 1.66 - 0.25 = 1.41 V**

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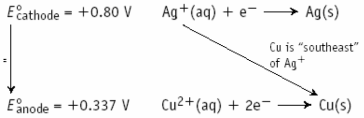
Calculating E°

Calculate E°_{net} for reaction between Cu and Ag^+ ions



$Ag^+ + e^- \rightarrow Ag$ $E^\circ = 0.80$ V

$Cu^{2+} + 2\,e^- \rightarrow Cu$ $E^\circ = 0.337$ V

*Ag^+ ok as written; need to **flip** Cu^{2+} reaction to:*

$Cu \rightarrow Cu^{2+} + 2\,e^-$ $E^\circ = -0.337$ V

E^o_{net} *for Cu/Ag+ reaction* **= 0.80 - 0.337 =** +0.46 V

balanced reaction: $Cu + 2\,Ag^+ \rightarrow 2\,Ag + Cu^{2+}$

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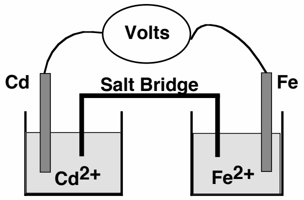
E° for a Voltaic Cell



$Cd \rightarrow Cd^{2+} + 2e^-$	*and*	**$Fe^{2+} + 2e^- \rightarrow Fe$**
or		*or*
$Cd^{2+} + 2e^- \rightarrow Cd$	*and*	**$Fe \rightarrow Fe^{2+} + 2e^-$**

All ingredients are present.
Which way does the reaction proceed?

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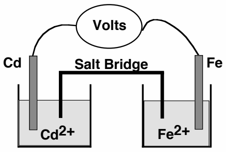
E° for a Voltaic Cell



From tables, you see:

$Fe^{2+} + 2\,e^- \rightarrow Fe$ $E^\circ = -.40$

$Cd^{2+} + 2\,e^- \rightarrow Cd$ $E^\circ = -.44$

Reaction occurs spontaneously when E° values are positive

Overall reaction:

$Fe^{2+} + Cd \rightarrow Cd^{2+} + Fe$

$E^o = E^\circ_{cathode} - E^\circ_{anode}$

$= (-0.40\text{ V}) - (-0.44\text{ V})$

$= +0.04$ V

MAR

More About Calculating Cell Voltage

Can I^- ion reduce water? From tables:

$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$ $E^\circ = -.828$ V

$2\,I^- \rightarrow I_2 + 2e^-$ $E^\circ = -.535$ V

$2\,I^- + 2\,H_2O \rightarrow I_2 + 2\,OH^- + H_2$

Assuming reaction occurs as written,

$E^\circ_{net} = E^\circ_{red} + E^\circ_{ox} = -0.828\text{ V} - 0.535\text{ V} =$ -1.363 V

Minus E° means rxn occurs in opposite direction!

$I_2 + 2OH^- + H_2 \rightarrow 2I^- + 2H_2O$ $E^\circ = +1.363$ V

I^- ion does not reduce water spontaneously!

MAR

More About Calculating Cell Voltage

Can we *make* the I^- ion reduce water?

$2\,I^- + 2\,H_2O \rightarrow I_2 + 2\,OH^- + H_2$ $E^\circ = -1.363$ V

Non-spontaneous (negative E°) reactions can be "forced" to occur with external voltage

Voltage can be applied through battery, other voltaic cells, etc.

Applying 1.363 V **to the above** electrolytic cell **will cause the I^- reduce water -** electrolysis

Are we cheating the second law of thermodynamics?

MAR

E° and ΔG°

E° is related to ΔG°, the free energy change for the reaction.

$$\Delta G^\circ = -\,n\,F\,E^\circ$$

where F = Faraday constant
$= 9.6485 \times 10^4$ C/mol e^-

and n is the number of moles of electrons transferred

Michael Faraday
1791-1867

***Memorize* the value of F!**

Always use 96485 for F!

MAR

E° and ΔG°

$$\Delta G^\circ = -nFE^\circ$$

For a product-favored reaction

Reactants → Products

$\Delta G^\circ < 0$ and so $E^\circ > 0$

E° is positive

For a reactant-favored reaction

Reactants ← Products

$\Delta G^\circ > 0$ and so $E^\circ < 0$

E° is negative

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Quantitative Aspects of Electrochemistry

Consider electrolysis of aqueous silver ion.

$Ag^+(aq) + e^- \rightarrow Ag(s)$

1 mol e- → 1 mol Ag

If we could measure the moles of e-, we could know the quantity of Ag formed.

But how to measure moles of e-?

$$\text{Current} = \frac{\text{charge passing}}{\text{time}} \qquad \text{I (amps)} = \frac{\text{coulombs}}{\text{seconds}}$$

MAR

Quantitative Aspects of Electrochemistry

$$\text{Amps} = \frac{\text{coulombs}}{\text{seconds}}$$

A current of 1.50 amps (1.50 C/s) flows through a $Ag^+(aq)$ solution for 15.0 min. What mass of Ag metal is deposited?

Solution

(a) Calculate charge in Coulombs (C)

1.50 amps = 1.50 C/s

= (1.50 C/s)(60 s/min)(15.0 min) = 1350 C

MAR

Quantitative Aspects of Electrochemistry

$$\text{Amps} = \frac{\text{coulombs}}{\text{seconds}}$$

A current of 1.50 amps (1.50 C/s) flows through a $Ag^+(aq)$ solution for 15.0 min. What mass of Ag metal is deposited?

Solution

(a) Charge = 1350 C

(b) Calculate moles of e- used *(F = 96,485 C/mol e-)*

$$1350\text{ C} \cdot \frac{1\text{ mol e-}}{96{,}485\text{ C}} = 0.0140\text{ mol e-}$$

(c) Calc. quantity of Ag

$$0.0140\text{ mol e-} \cdot \frac{1\text{ mol Ag}}{1\text{ mol e-}} = 0.0140\text{ mol Ag or }1.51\text{ g Ag}$$

MAR

Quantitative Aspects of Electrochemistry

The *anode reaction* in a lead storage battery is

$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$

If a battery delivers 1.50 amp, and you have 454 g of Pb, how long will the battery last?

Solution

a) 454 g Pb = 2.19 mol Pb

b) Calculate moles of e-

$$2.19\text{ mol Pb} \cdot \frac{2\text{ mol e-}}{1\text{ mol Pb}} = 4.38\text{ mol e-}$$

c) Calculate charge

4.38 mol e- • 96,485 C/mol e- = 423,000 C

MAR

Quantitative Aspects of Electrochemistry

The anode reaction in a lead storage battery is

$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$

If a battery delivers 1.50 amp, and you have 454 g of Pb, how long will the battery last?

Solution

a) 454 g Pb = 2.19 mol Pb

b) Mol of e- = 4.38 mol

c) Charge = 423,000 C

d) Calculate time $\text{Time } (s) = \frac{\text{Charge (C)}}{\text{I (amps)}}$

$$\text{Time } (s) = \frac{423{,}000\text{ C}}{1.50\text{ amp}} = 282{,}000\text{ s}$$ **About 78.3 hours**

MAR

The Nernst Equation

Q, the reaction quotient, can be related to non standard cell potentials, E

E is related to Q, the reaction quotient, by:

$$E = E° - (RT/nF) \ln Q$$

where R = Gas constant (8.3145 J/K mol)
T = Temperature (K)
F = Faraday constant
E° = standard cell potential
and n = the number of moles of electrons transferred

This is the Nernst Equation (<u>Handout</u>)

MAR

The Nernst Equation

$Cu^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cu(s)$

For Zn/Cu cell, voltage is 1.10 V at 25 ˚C when $[Zn^{2+}]$ and $[Cu^{2+}]$ = 1.0 M

Adding $Cu^{2+}_{(aq)}$ shifts reaction right (Le Chatelier's Principle), making reaction more spontaneous (∆G) and E° more positive

MAR

The Nernst Equation

Example: Find E when $[Zn^{2+}]$ = 0.0010 M, $P(H_2)$ = 0.10 atm and pH = 0 at 290. K.

Solution: *Find E° for reaction under standard conditions first*

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e-$ E° = 0.76 V
$2 H^+(aq) + 2e- \longrightarrow H_2(g)$ E° = 0.00 V
--
$2 H^+(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + H_2(g)$
$E°_{net}$ = 0.76 V

Note that n = 2

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The Nernst Equation

Example: Find E when $[Zn^{2+}]$ = 0.0010 M, $P(H_2)$ = 0.10 atm and pH = 0 at 290. K. $[H^+]$ = 1.0 M

$2 H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)$ $E°_{net}$ = 0.76 V

Solution

Use Nernst Equation:

$E = E° - (RT/nF) \ln Q$
$E = 0.76 V - (8.3145 * 290. K / 2 * 96485) \ln Q$
$[H^+] = 10^{-pH} M = 10^{-0} M = 1.0 M$
$Q = [Zn^{2+}] * P_{H2} / [H^+]^2 = [0.0010 * 0.10 / (1.0)^2]$

E = 0.76 V + 0.12 V = 0.88 V

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E° and K

At Equilibrium (K), combine ∆G expressions for E° and K to get:

$$E^\circ = \frac{RT}{nF} \ln K$$

***If at 298 K*, can use:**

$$E^\circ = \frac{0.0257}{n} \ln K$$

Only valid at 298 K!
Find equilibrium constants from E˚ data!

MAR

Electrochemical Processes in Batteries

A **battery** consists of self-contained voltaic cells arranged in series, so their individual voltages are added.

A **primary battery** cannot be recharged. The battery is "dead" when the cell reaction has reached equilibrium.

A **secondary battery** is rechargeable. Once it has run down, electrical energy is supplied to reverse the cell reaction and form more reactant.

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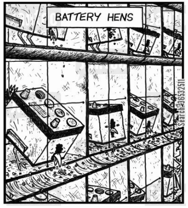

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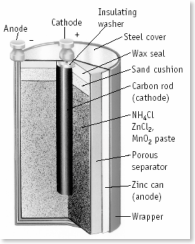


Dry Cell Battery

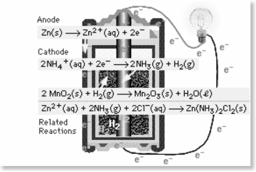
A primary battery - uses reactions that cannot be recharged

Anode (-)

$Zn \rightarrow Zn^{2+} + 2e-$

Cathode (+)

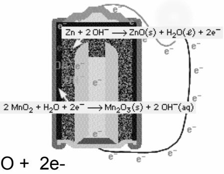
$2\ NH_4^+ + 2e- \rightarrow$
$2\ NH_3 + H_2$



MAR

Alkaline Battery

Nearly same reactions as in common dry cell, but under basic conditions.



Anode (-): $Zn + 2\ OH^-$ ---> $ZnO + H_2O + 2e-$

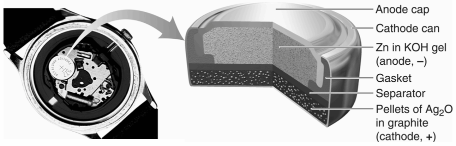
Cathode (+): $2\ MnO_2 + H_2O + 2e-$ ---> $Mn_2O_3 + 2\ OH^-$

$Zn(s) + MnO_2(s) + H2O(l) \rightarrow ZnO(s) + Mn(OH)_2(s)$

$E_{cell} = 1.5$ V

MAR

Silver Button Battery



Anode (oxidation): $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode (reduction): $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Overall (cell) reaction: $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$

$E_{cell} = 1.6$ V

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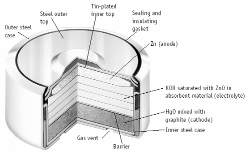
Mercury Button Battery

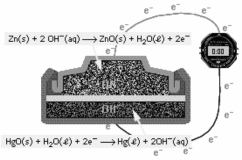
Anode:

Zn is reducing agent under basic conditions

Cathode:

$HgO + H_2O + 2e- \rightarrow Hg + 2\ OH^-$





MAR

Lead-Acid Storage Battery

Anode (0.36 V): $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$

Cathode (1.68 V):

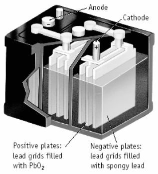
$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall (cell) reaction (discharge):

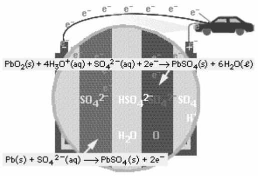
$PbO_2(s) + Pb(s) + H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$ $E_{cell} = 2.04$ V

Overall (cell) reaction (recharge):

$2PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + Pb(s) + H_2SO_4(aq)$

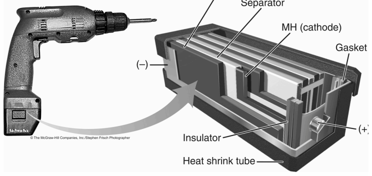


A secondary battery - can be recharged, reversible redox reactions



MAR

Nickel-Cadmium Battery



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Anode (-):

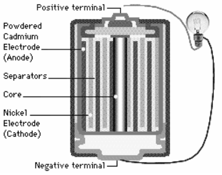
$Cd + 2\ OH^- \rightarrow Cd(OH)_2 + 2e-$

Cathode (+):

$NiO(OH) + H_2O + e- \rightarrow$
$Ni(OH)_2 + OH^-$

Overall cell:

$2\ NiO(OH) + 2\ H_2O + Cd \rightarrow$
$2\ Ni(OH)_2 + Cd(OH)_2$
$E_{cell} = 1.4$ V



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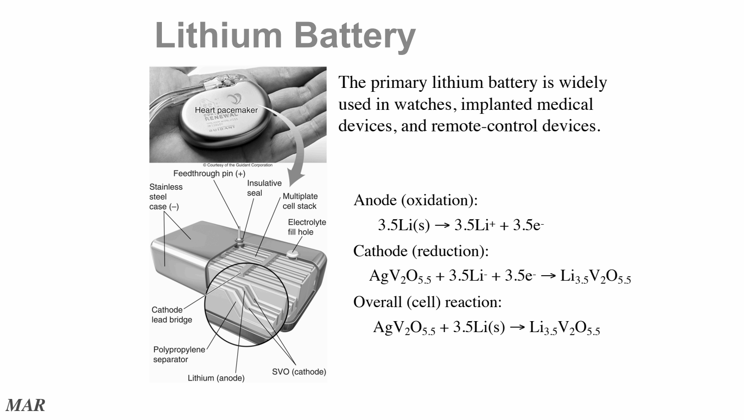


Lithium Battery

The primary lithium battery is widely used in watches, implanted medical devices, and remote-control devices.

Anode (oxidation):

$3.5Li(s) \rightarrow 3.5Li^{+} + 3.5e^{-}$

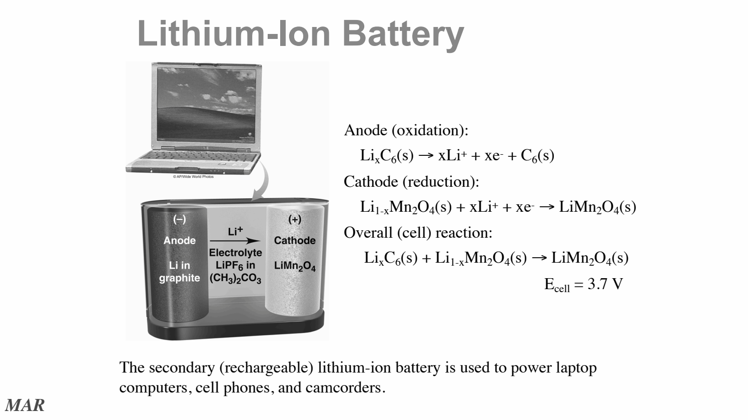
Cathode (reduction):

$AgV_2O_{5.5} + 3.5Li^{-} + 3.5e^{-} \rightarrow Li_{3.5}V_2O_{5.5}$

Overall (cell) reaction:

$AgV_2O_{5.5} + 3.5Li(s) \rightarrow Li_{3.5}V_2O_{5.5}$

MAR



Lithium-Ion Battery

Anode (oxidation):

$Li_xC_6(s) \rightarrow xLi^{+} + xe^{-} + C_6(s)$

Cathode (reduction):

$Li_{1-x}Mn_2O_4(s) + xLi^{+} + xe^{-} \rightarrow LiMn_2O_4(s)$

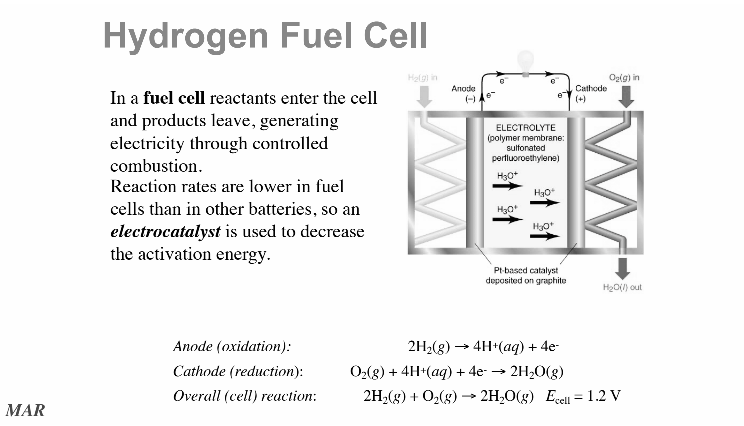
Overall (cell) reaction:

$Li_xC_6(s) + Li_{1-x}Mn_2O_4(s) \rightarrow LiMn_2O_4(s)$

$E_{cell} = 3.7$ V

The secondary (rechargeable) lithium-ion battery is used to power laptop computers, cell phones, and camcorders.

MAR



Hydrogen Fuel Cell

In a **fuel cell** reactants enter the cell and products leave, generating electricity through controlled combustion.

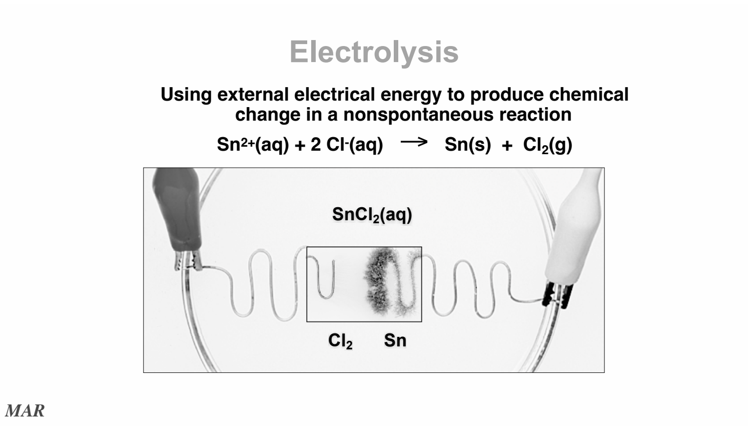
Reaction rates are lower in fuel cells than in other batteries, so an ***electrocatalyst*** is used to decrease the activation energy.

Anode (oxidation): $2H_2(g) \rightarrow 4H^{+}(aq) + 4e^{-}$

Cathode (reduction): $O_2(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(g)$

Overall (cell) reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $E_{cell} = 1.2$ V

MAR

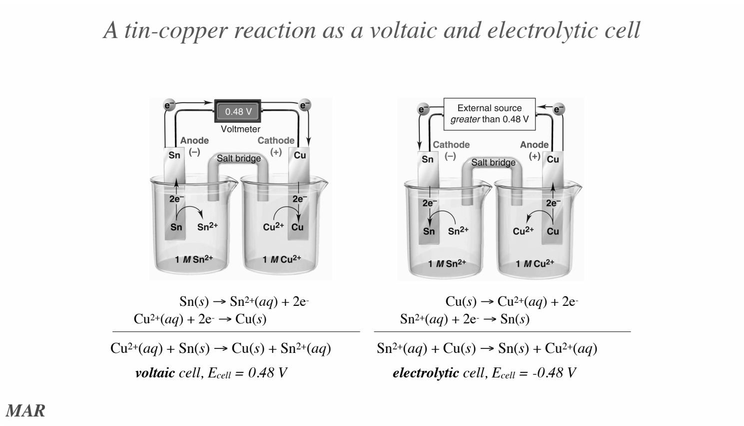


Electrolysis

Using external electrical energy to produce chemical change in a nonspontaneous reaction

$Sn^{2+}(aq) + 2\,Cl^{-}(aq) \longrightarrow Sn(s) + Cl_2(g)$

MAR



A tin-copper reaction as a voltaic and electrolytic cell

$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^{-}$

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

$Cu^{2+}(aq) + Sn(s) \rightarrow Cu(s) + Sn^{2+}(aq)$

***voltaic** cell, $E_{cell} = 0.48$ V*

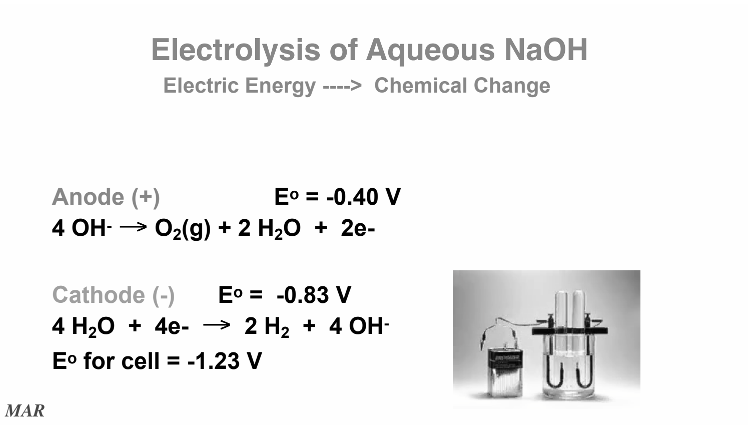
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$

$Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$

$Sn^{2+}(aq) + Cu(s) \rightarrow Sn(s) + Cu^{2+}(aq)$

***electrolytic** cell, $E_{cell} = -0.48$ V*

MAR



Electrolysis of Aqueous NaOH

Electric Energy ----> Chemical Change

Anode (+) **$E^{o} = -0.40$ V**

$4\,OH^{-} \longrightarrow O_2(g) + 2\,H_2O + 2e-$

Cathode (-) **$E^{o} = -0.83$ V**

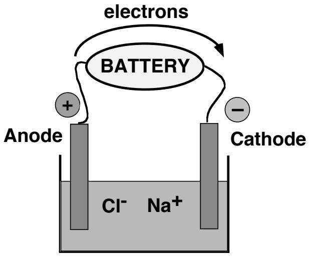
$4\,H_2O + 4e- \longrightarrow 2\,H_2 + 4\,OH^{-}$

E^{o} for cell = -1.23 V

MAR

Electrolysis

Electric Energy ---> Chemical Change

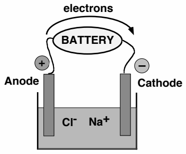


Electrolysis of molten NaCl. Here a battery "pumps" electrons from Cl^- to Na^+.

Polarity of electrodes is reversed from batteries.

MAR

Electrolysis of Molten NaCl



Anode (+) **$E^o = -1.36$ V**

$2\ Cl^- \rightarrow Cl_2(g) + 2e^-$

Cathode (-) **$E^o = -2.71$ V**

$Na^+ + e^- \rightarrow Na$

E^o for cell = -4.07 V

External energy needed because E^o is (-).

MAR

Electrolysis of Aqueous NaCl

Anode (+) **$E^o = -1.36$ V**

$2\ Cl^- \rightarrow Cl_2(g) + 2e^-$

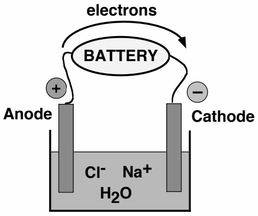
Cathode (-) **$E^o = -0.83$ V**

$2\ H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$

E^o for cell = -2.19 V

Note that H_2O is more easily reduced than Na^+.

Also, Cl^- is oxidized in preference to H_2O because of kinetics.



MAR

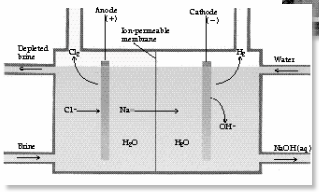
Electrolysis of Aqueous NaCl

Cells like these are the source of NaOH and Cl_2.

In 2006

65 million tons Cl_2

81 million tons NaOH

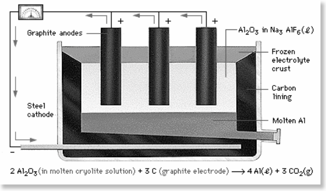


Also the source of NaOCl for use in bleach.

MAR

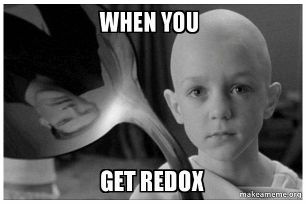
Producing Aluminum

$2\ Al_2O_3 + 3\ C \rightarrow 4\ Al + 3\ CO_2$



Charles Hall (1863-1914) developed electrolysis process, founded Alcoa *(alcoa.com)*

MAR



See:

- *Chapter Seventeen Study Guide*
- *Chapter Seventeen Concept Guide*
- *Types of Equilibrium Constants*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*

End of Chapter 17

MAR

Important Equations, Constants, and Handouts from this Chapter:

Redox Reactions: **oxidation, reduction, LEO, GER, oxidizing agent, reducing agent, anode, cathode, galvanic/voltaic cells, electrolysis (electrolytic cells), shorthand notation for galvanic cells, SHE electrode**

- **know how to balance redox reactions in acid or base conditions**
- **be able to calculate E° and E for cells**

$$\Delta G^\circ = -nFE^\circ$$

$$\text{Amps} = \frac{\text{coulombs}}{\text{seconds}}$$

$$E = E^\circ - (RT/nF)\ln Q$$

$R = 8.3145\ J\ mol^{-1}\ K^{-1}$

F = 9.6485 x 10^4 C/mol e^-

$$E^\circ = \frac{RT}{nF}\ln K$$

Handouts:

- *Thermodynamic Values and Electrochemical Cell Values (Problem Set #5)*

MAR

End of Chapter Problems: *Test Yourself*

You will need the table of reduction potentials found in problem set #5

1. Write a balanced equation for the following half-reaction: **VO_3^{-1}(aq) → V^{2+}(aq) (in acid)**
2. Write a balanced equation for the following half-reaction: **Ag(s) → Ag_2O(s) (in base)**
3. Balance the following redox equation in acid: **Zn(s) + NO_3^{-1}(aq) → Zn^{2+}(aq) + N_2O(g)**
4. Balance the following redox equation in base: **CrO_4^{2-}(aq) + SO_3^{2-}(aq) → $Cr(OH)_3$(s) + SO_4^{2-}(aq)**
5. Balance the following *unbalanced* equation in acid, then calculate the standard redox potential, *E°:* **Cu(s) + NO_3^{-1}(aq) → Cu^{2+}(aq) + NO(g)**
6. Calculate *E°, ΔG°* and the equilibrium constant for the following reaction: 2 Fe^{3+}(aq) + 2 I^{-1}(aq) → 2 Fe^{2+}(aq) + I_2(aq)

MAR

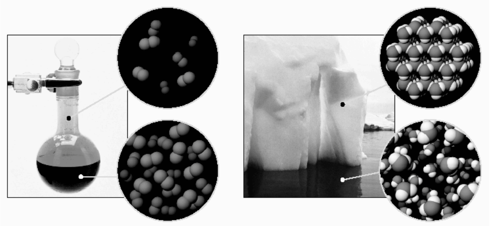
End of Chapter Problems: *Answers*

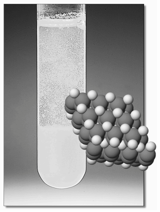
1. VO_3^-(aq) + 6 H^+(aq) + 3 e^- → V^{2+}(aq) + 3 H_2O(l)
2. 2 Ag(s) + 2 OH^-(aq) → Ag_2O(s) + H_2O(l) + 2 e^-
3. 4 Zn(s) + 2 NO_3^-(aq) + 10 H^+(aq) → 5 H_2O(l) + 4 Zn^{2+}(aq) + N_2O(g)
4. 2 CrO_4^{2-}(aq) + 5 H_2O(l) + 3 SO_3^{2-}(aq) → 2 $Cr(OH)_3$(s) + 4 OH^-(aq) + 3 SO_4^{2-}(aq)
5. 3 Cu(s) + 2 NO_3^{-1}(aq) + 8 H^+(aq) → 2 NO(g) + 3 Cu^{2+}(aq) + 4 H_2O(l), *E°* = 0.62 V
6. *E°* = 0.236 V, Δ*G°* = -45.5 kJ, K = 9 x 10^7

You will need the table of reduction potentials found in problem set #5

MAR

Chemistry 223 Exam II Review
Chapters 15, 16 and 17





Chemistry 223
Professor Michael Russell

Last update: 4/29/24

MAR

Decide if a precipitate will form when mixing the indicated reagents (all concentrations are 1.0 M).

$KCl(aq) + Pb(NO_3)_2(aq) \rightarrow ?$

A. Yes
B. No
C. Who knows!

MAR

If the solubility of BaF_2 is 3.6×10^{-3}, a reasonable value for K_{sp} for BaF_2 is

A. 3.6×10^{-3}
B. 7.2×10^{-3}
C. 1.1×10^{-2}
D. 1.9×10^{-7}
E. 4.7×10^{-8}

MAR

Which lead salt has the greatest molar solubility in water at 25 °C?

A. $PbCO_3$	$K_{sp} = 1.5 \times 10^{-13}$
B. PbS	$K_{sp} = 8.4 \times 10^{-28}$
C. $PbSO_4$	$K_{sp} = 1.8 \times 10^{-4}$

MAR

A solution contains 0.10 M K_2SO_3 and 0.30 M Na_2SO_4. Solid $Ca(NO_3)_2$ is added slowly. Which precipitates first, $CaSO_3$ or $CaSO_4$?

K_{sp} for $CaSO_3 = 1.3 \times 10^{-8}$
K_{sp} for $CaSO_4 = 2.4 \times 10^{-5}$

A. $CaSO_3$
B. $CaSO_4$
C. 42

MAR

$CaSO_3$ precipitates first as Ca^{2+} ions are added to a solution containing 0.10 M K_2SO_3 and 0.30 M Na_2SO_4. What is $[SO_3^{2-}]$ as the $CaSO_4$ begins to precipitate?

$K_{sp}(CaSO_3) = 1.3 \times 10^{-8}$ $K_{sp}(CaSO_4) = 2.4 \times 10^{-5}$

A. 0.10 M
B. 0.30 M
C. 1.6×10^{-4} M
D. 5.4×10^{-4} M
E. 42

MAR

What is the pH of a saturated solution of $Mg(OH)_2$? (K_{sp} ($Mg(OH)_2$) = 5.6×10^{-12})

A. 3.65
B. 8.37
C. 10.35
D. 0.15
E. 11.25

MAR

A solution has $[Pb^{2+}]$ = 0.0012 M and $[Cl^-]$ = 0.010 M. Will $PbCl_2$ precipitate? K_{sp} ($PbCl_2$) = 1.7×10^{-5}

A. Yes, $PbCl_2$ precipitates
B. No, $PbCl_2$ does NOT precipitate

MAR

Which of the following shows the correct formation constant (*K_f*) equation for $Cr(CN)_6^{3-}$?

A. $Cr(CN)_3(s) + 3\ CN^{-1}(aq) \rightleftarrows Cr(CN)_6^{3-}(aq)$
B. $Cr(NO_3)_3(s) + 6\ NaCN(aq) \rightleftarrows Cr(CN)_6^{3-}(aq) + 3\ NaNO_3(aq) + 3\ Na^+(aq)$
C. $Cr(CN)_6^{3-}(s) \rightleftarrows Cr^{3+}(aq) + 6\ CN^{-1}(aq)$
D. $Cr(CN)_6^{3-}(aq) \rightleftarrows Cr^{3+}(aq) + 6\ CN^{-1}(aq)$
E. $Cr^{3+}(aq) + 6\ CN^{-1}(aq) \rightleftarrows Cr(CN)_6^{3-}(aq)$

MAR

Calculate the standard entropy change for the following reaction:

$$\mathbf{CCl_4(l) + O_2(g) \rightarrow CO_2(g) + 2\ Cl_2(g)}$$

* S°[CCl_4(l)] = 214.39 J/K • mol
* S°[CO_2(g)] = 213.74 J/K • mol
* S°[O_2(g)] = 205.07 J/K • mol
* S°[Cl_2(g)] = 223.08 J/K • mol

A. -17.36 J/K
B. +17.36 J/K
C. +240.44 J/K
D. -25.78 J/K
E. 42

MAR

Calculate $\Delta G_{rxn}°$ for the following reaction:

$$\mathbf{CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)}$$

* $\Delta G_f°$[CO_2(g)] = -394.4 kJ/mol
* $\Delta G_f°$[CH_4(g)] = -50.8 kJ/mol
* $\Delta G_f°$[H_2O(g)] = -228.6 kJ/mol

A. 572.2 kJ/mol•rxn
B. -673.7 kJ/mol•rxn
C. -572.2 kJ/mol•rxn
D. -436.4 kJ/mol•rxn
E. -800.8 kJ/mol•rxn

MAR

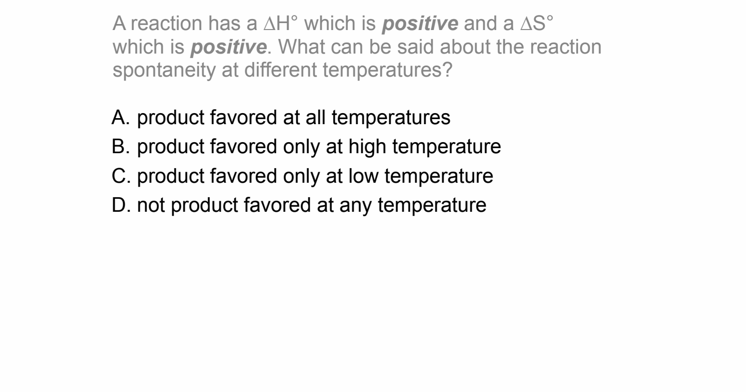
Given the following information, calculate ΔG° for the reaction below at 25 °C:

$$\mathbf{Mg(s) + 1/2\ O_2(g) \rightarrow MgO(s)}$$

ΔH° = -601.24 kJ/mol•rxn
ΔS° = -108.36 J/K•rxn

A. 664.5 kJ/mol•rxn
B. -568.9 kJ/mol•rxn
C. 31700 kJ/mol•rxn
D. -528.3 kJ/mol•rxn
E. 42

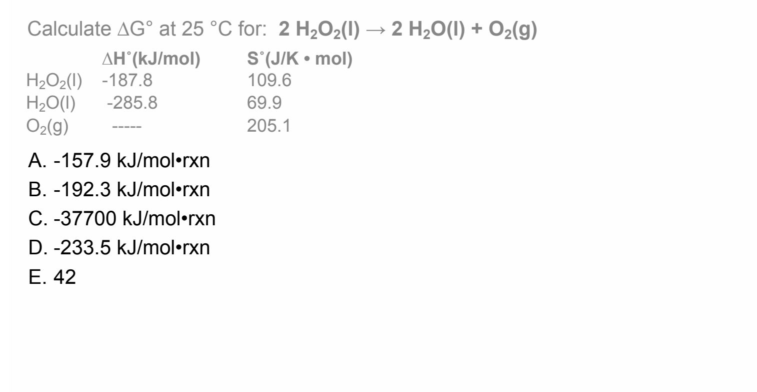
MAR



A reaction has a ΔH° which is ***positive*** and a ΔS° which is ***positive***. What can be said about the reaction spontaneity at different temperatures?

A. product favored at all temperatures
B. product favored only at high temperature
C. product favored only at low temperature
D. not product favored at any temperature

MAR

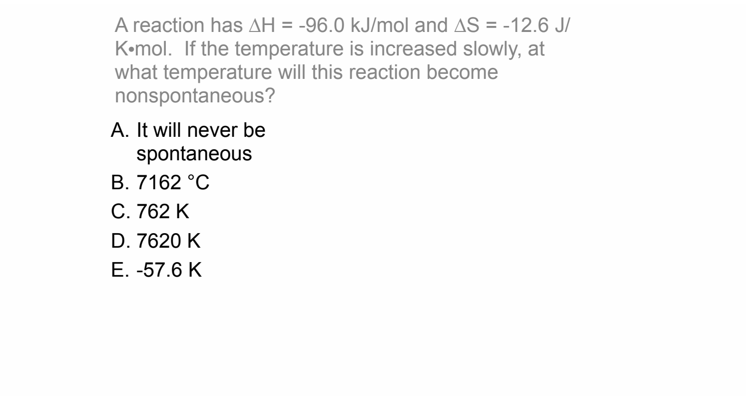


Calculate ΔG° at 25 °C for: **$2\ H_2O_2(l) \rightarrow 2\ H_2O(l) + O_2(g)$**

	ΔH˚(kJ/mol)	**S˚(J/K • mol)**
$H_2O_2(l)$	-187.8	109.6
$H_2O(l)$	-285.8	69.9
$O_2(g)$	-----	205.1

A. -157.9 kJ/mol•rxn
B. -192.3 kJ/mol•rxn
C. -37700 kJ/mol•rxn
D. -233.5 kJ/mol•rxn
E. 42

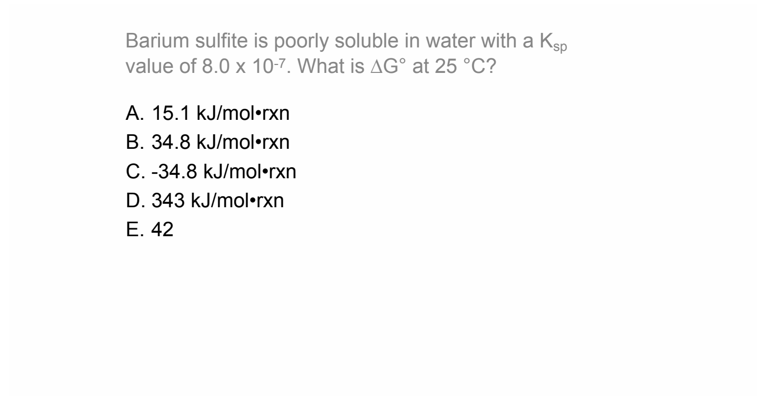
MAR



A reaction has ΔH = -96.0 kJ/mol and ΔS = -12.6 J/K•mol. If the temperature is increased slowly, at what temperature will this reaction become nonspontaneous?

A. It will never be spontaneous
B. 7162 °C
C. 762 K
D. 7620 K
E. -57.6 K

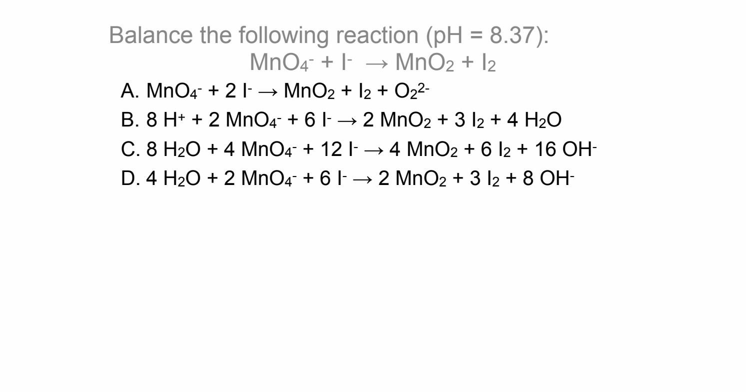
MAR



Barium sulfite is poorly soluble in water with a K_{sp} value of 8.0×10^{-7}. What is ΔG° at 25 °C?

A. 15.1 kJ/mol•rxn
B. 34.8 kJ/mol•rxn
C. -34.8 kJ/mol•rxn
D. 343 kJ/mol•rxn
E. 42

MAR

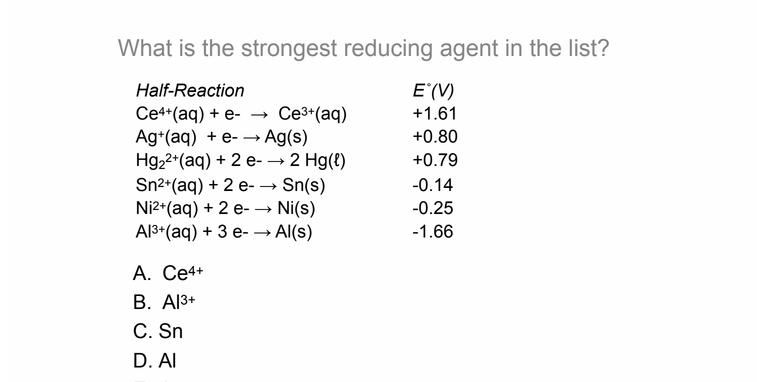


Balance the following reaction (pH = 8.37):

$MnO_4^- + I^- \rightarrow MnO_2 + I_2$

A. $MnO_4^- + 2\ I^- \rightarrow MnO_2 + I_2 + O_2^{2-}$
B. $8\ H^+ + 2\ MnO_4^- + 6\ I^- \rightarrow 2\ MnO_2 + 3\ I_2 + 4\ H_2O$
C. $8\ H_2O + 4\ MnO_4^- + 12\ I^- \rightarrow 4\ MnO_2 + 6\ I_2 + 16\ OH^-$
D. $4\ H_2O + 2\ MnO_4^- + 6\ I^- \rightarrow 2\ MnO_2 + 3\ I_2 + 8\ OH^-$

MAR



What is the strongest reducing agent in the list?

Half-Reaction	*E˚(V)*
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Hg_2^{2+}(aq) + 2\ e^- \rightarrow 2\ Hg(\ell)$	+0.79
$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$	-0.14
$Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$	-0.25
$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$	-1.66

A. Ce^{4+}
B. Al^{3+}
C. Sn
D. Al
E. Jq

MAR

Will Sn(s) reduce $Ag^+(aq)$ to Ag(s)?

Half-Reaction	*E˚(V)*
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$	-0.14

A. Yes
B. No
C. Only if it feels like it

MAR

Determine the equilibrium constant for the following reaction at 25 °C:

$Cl_2(aq) + 2I^-(aq) \rightarrow 2\ Cl^-(aq) + I_2(aq)$ E° = +0.825 V

A. 1.31×10^{-28}
B. 8.74×10^{13}
C. 8.03×10^{27}
D. 0.217
E. -1.16×10^{5}

MAR

A **voltaic** cell is created using the information below to be used in Alaska where the average temperature is 5.00 °C. Calculate the expected cell potential under these conditions.

$Al(s)\ |\ Al^{3+}(aq,\ 0.0010\ M)\ ||\ Ni^{2+}(aq,\ 0.50\ M)\ |\ Ni(s)$

$Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$	-0.25 V
$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$	-1.66 V

A. 1.46 V
B. 1.31 V
C. 1.17 V
D. 0.51 V
E. -1.91 V

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How long must a 2.00 amp current flow through a gold solution to convert 0.0100 mol of $Au^{3+}(aq)$ into Au(s)?

A. 483 s
B. 4.83×10^4 s
C. 965 s
D. 1450 s
E. 1 zillion s

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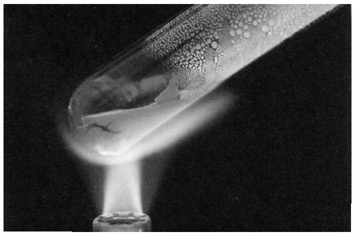
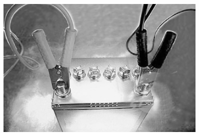
End of Review - *good luck with your studying!*



Need more practice?

- *Practice Problem Sets (online)*
- *Concept Guides (Companion and online)*
- *Chapter Guides (online)*
- *End of Chapter Problems in Textbook (every other question has answer at end)*

Good luck with your studying!



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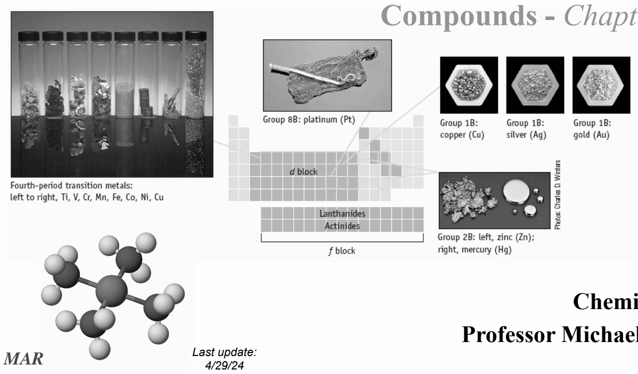
Chemistry of Coordination Compounds - *Chapter 19*



Fourth-period transition metals: left to right, Ti, V, Cr, Mn, Fe, Co, Ni, Cu

Chemistry 223
Professor Michael Russell

MAR

Last update: 4/29/24

Color Theory

Where does the color of objects come from?

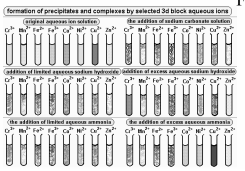
From the paint covering the object!

Where does the paint gets its color?

From the paint pigments!

What are the pigments?

Colorful transition metal compounds!



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Why Study Transition Metals

- Transition metals found in nature
  - Rocks and minerals contain transition metals
    - Red rubies (Cr), blue sapphires (Fe and Ti)
  - Many biomolecules contain transition metals
    - Vitamin B12 (Co), Hemoglobin, myoglobin, and cytochrome C (all Fe)
- Transition metals used in industry
  - Material science (steel, alloys)
  - Transition metal compounds are used as pigments
    - TiO_2 (white), $PbCrO_4$ (yellow), $Fe_4[Fe(CN)_6]_3$ (Prussian blue)

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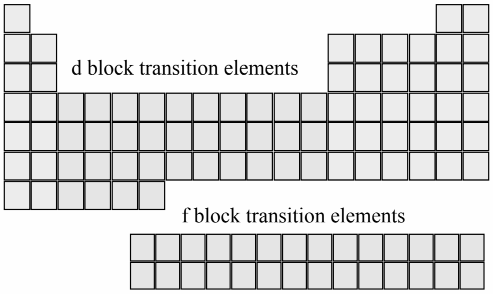
Periodic Table



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d-Block Transition Elements

IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB
Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**

Most have partially occupied d subshells in common oxidation states

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Transition Metals

- General Properties
  - Have typical metallic properties (malleable, etc.)
  - Not as reactive as alkali and alkaline earth metals
  - Have high melting points, high boiling points, high density
  - Have 1 or 2 *s* electrons in valence shell
  - Differ in # d electrons in n-1 energy level
  - Exhibit multiple oxidation states
  - Both paramagnetic and diamagnetic ions exist
  - Most ions deeply colored (crystal field theory)

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Electronic Configurations

Element	Configuration
Sc	[Ar]$3d^1 4s^2$
Ti	[Ar]$3d^2 4s^2$
V	[Ar]$3d^3 4s^2$
Cr	[Ar]$3d^5 4s^1$
Mn	[Ar]$3d^5 4s^2$
Fe	[Ar]$3d^6 4s^2$
Ni	[Ar]$3d^8 4s^2$
Cu	[Ar]$3d^{10} 4s^1$
Zn	[Ar]$3d^{10} 4s^2$

Oxidation States of Transition Elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
							+1	+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4		+4		
		+5	+5	+5	+5				
			+6	+6	+6				
				+7					

loss of ns e^-s

loss of ns and (n-1)d e^-s

Electronic Configurations of Transition Metal Ions

Electronic configuration of Fe ions:

$$Fe - 2e^- \rightarrow Fe^{2+}$$

valence *ns* electrons
removed first,
then *n-1 d* electrons

Paramagnetism and Diamagnetism

Paramagnetic species have unpaired electrons while **diamagnetic** species have all paired electrons

Paramagnetic species are attracted or repulsed by magnetic fields; the magnitude of the effect depends on the number of unpaired electrons

Examples:

Paramagnetic Cr [Ar] ↑ ↑ ↑ ↑ ↑ (3 d) ↑ (4s)

Diamagnetic Pd [Kr] ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ (4 d) ☐ (5s)

Coordination Chemistry

Transition metals act as **Lewis acids** and form **complexes** or **complex ions** with **Lewis bases** or **ligands**

$$\underset{\text{Lewis acid}}{Fe^{3+}(aq)} + \underset{\text{Lewis base}}{6\,CN^-(aq)} \rightarrow \underset{\text{Complex ion}}{Fe(CN)_6^{3-}(aq)}$$

$$\underset{\text{Lewis acid}}{Ni^{2+}(aq)} + \underset{\text{Lewis base}}{6\,NH_3(aq)} \rightarrow \underset{\text{Complex ion}}{Ni(NH_3)_6^{2+}(aq)}$$

Complex contains central metal ion bonded to one or more molecules or anions

Lewis acid = **metal** = center of coordination

Lewis base = **ligand** = molecules/ions covalently bonded to metal in complex

Coordination Chemistry

A **coordination compound** has one or more complexes.

Examples: $[Co(NH_3)_6]Cl_3$, $[Cu(NH_3)_4][PtCl_4]$, $[Pt(NH_3)_2Cl_2]$

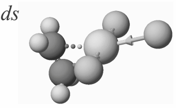
The **coordination number** is the number of donor atoms bonded to the central metal atom or ion in the complex.

Example: $[Co(NH_3)_6]^{3+}$ coordination number = **6**

Example: $[PtCl_4]^{2-}$ coordination number = **4**

Most common = 6, 4 *and* 2

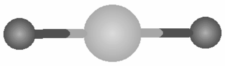
Coordination number determined by ligands



Common Geometries of Complexes

Coordination Number — Geometry

2



Linear

Example: $[Ag(NH_3)_2]^+$

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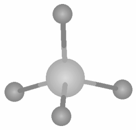
Common Geometries of Complexes

Coordination Number — Geometry

4 — tetrahedral

(most common)



Examples: $[Zn(NH_3)_4]^{2+}$, $[FeCl_4]^-$

and

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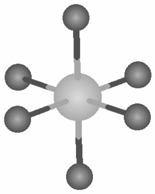
Common Geometries of Complexes

Coordination Number — Geometry

6

(most common of all metal coordination numbers)



Examples: $[Co(CN)_6]^{3-}$, $[Fe(en)_3]^{3+}$

octahedral

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Coordination Chemistry

Charge of **complex** = sum of charges on the metal and the ligands

Charge of coordination **compound** = sum of charges on metal, ligands, and counterbalancing ions

$[Fe(CN)_6]^{3-}$

+3 — 6(-1)

anionic ***complex***

$[Co(NH_3)_6]Cl_2$

+2 — 6(0) — 2(-1)

neutral ***compound***

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Coordination Chemistry

Ligands - *aka Lewis bases*

- classified according to the number of bonds to central metal
- **"dentate"** = "tooth"
- Examples
  - **monodentate** = 1
  - **bidentate** = 2
  - **tetradentate** = 4
  - **hexadentate** = 6
  - **polydentate** = 2 or more donor atoms

chelating agents

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Monodentate Ligands

Monodentate ligands possess only one accessible donor group.

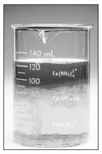
H_2O is a good example since *all* metal ions exist as *aqua* complexes in water

Monodentate Ligand Examples:

- **H_2O, CN^-, NH_3, NO_2^-, SCN^-, OH^-, X^- (halides), CO, O^{2-}**

Example Complexes:

- $[Co(NH_3)_6]^{3+}$
- $[Fe(SCN)_6]^{3-}$



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Bidentate Ligands

Bidentate Ligands have "two teeth", able to bond with metal at two separate places

Bidentate Examples:

- **oxalate ion = $C_2O_4^{2-}$**
- **ethylenediamine (en) = $NH_2CH_2CH_2NH_2$**
- **ortho-phenanthroline (o-phen)**

Example Complexes:

- $[Co(en)_3]^{3+}$
- $[Cr(C_2O_4)_3]^{3-}$
- $[Fe(NH_3)_4(o\text{-}phen)]^{3+}$

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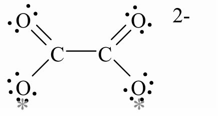
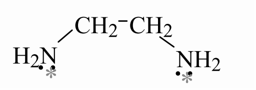
Bidentate Ligands

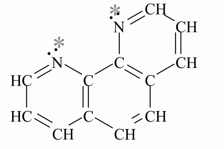
oxalate ion (ox)



ethylenediamine (en)



ortho-phenanthroline (o-phen)



Donor Atoms

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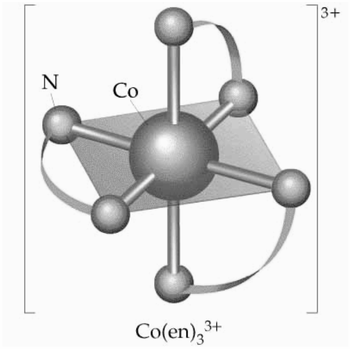
Bidentate Ligands



$Co(en)_3^{3+}$

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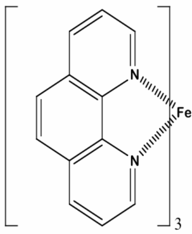
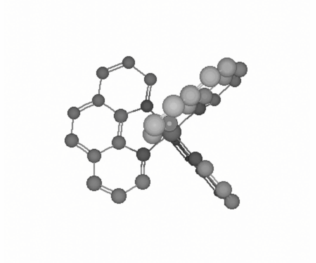
Bidentate Ligands

$Fe(o\text{-}phen)_3^{2+}$:





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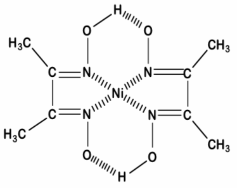
Bidentate Ligands

Another bidentate ligand:
Dimethylglyoxime (dmg)

$Ni(dmg)_2$ *(from lab)*:



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EDTA

A commonly used *polydentate* ligand

Forms 1:1 complexes with most metals except Group IA

Forms stable, water soluble complexes

High formation constants

A *primary standard* material

See the movie "Blade" (!)

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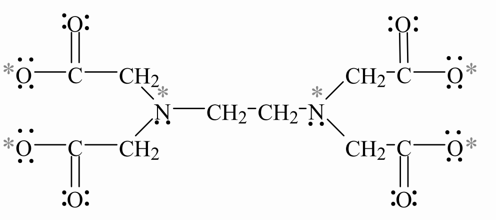
EDTA

Six Donor Regions



EDTA (Ethylenediamine tetraacetic acid) will adapt its coordination number to bond with the metal

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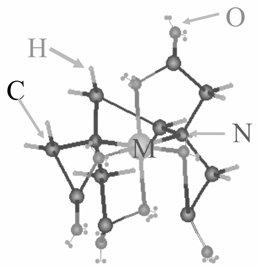
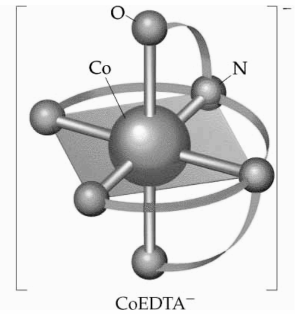
EDTA





$CoEDTA^-$

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EDTA

Formation constants (K_f) for some metal - EDTA complexes.

Ion	log K	Ion	log K	Ion	log K
Fe^{3+}	25.1	Pb^{2+}	18.0	La^{3+}	15.4
Th^{4+}	23.2	Cd^{2+}	16.5	Mn^{2+}	14.0
Cr^{3+}	23.0	Zn^{2+}	16.5	Ca^{2+}	10.7
Bi^{3+}	22.8	Co^{2+}	16.3	Mg^{2+}	8.7
Cu^{2+}	18.8	Al^{3+}	16.1	Sr^{2+}	8.6
Ni^{2+}	18.6	Ce^{3+}	16.0	Ba^{2+}	7.8

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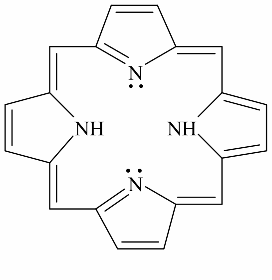
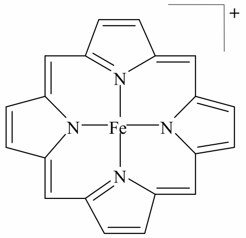
Other Chelating Agents

Porphine, an important chelating agent found in nature





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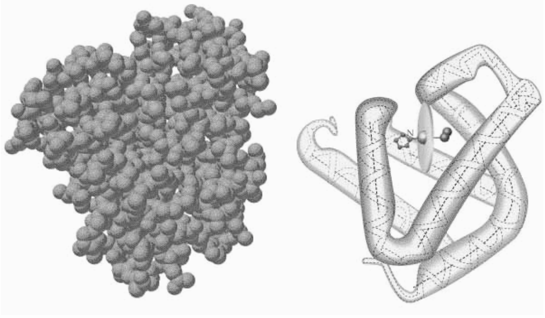
Myoglobin



Myoglobin, an Fe-containing protein that stores O_2 in cells

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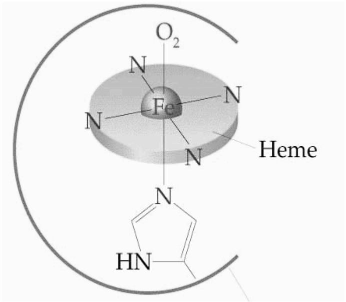
Coordination Environment of Fe^{2+} in Oxymyoglobin and Oxyhemoglobin



Oxymyoglobin

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Nomenclature of Coordination

The cation is named before the anion. When naming a complex:

- Cations named first, then anions. Anion metal gets *-ate* ending
- Ligands are named *first* in alphabetical order. Most ligands have *-o* ending; multiple ligands use Greek prefixes
- Metal atom/ion is named last with the oxidation state in Roman numerals.
- Use no spaces in complex name
- *See Coordination Compounds Handout*

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Nomenclature: IUPAC Rules

Neutral ligands are referred to by their usual name with these exceptions:

- water, H_2O = **aqua**
- ammonia, NH_3 = **ammine**
- carbon monoxide, CO = **carbonyl**
- hydroxide, OH^- = **hydroxo**

If the ligand name already contains a Greek prefix, use alternate prefixes for multiple occurrences:

- bis-, 2; tris-, 3; tetrakis-,4; pentakis-, 5; hexakis-, 6
- The name of the ligand is placed in parentheses; i.e. *bis(ethylenediamine)*

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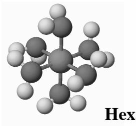
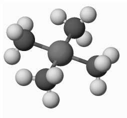
Nomenclature



$Co(H_2O)_6^{2+}$

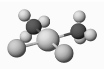
Hexaaquacobalt(II) ion

H_2O as a ligand is aqua



$Cu(NH_3)_4^{2+}$

Tetraamminecopper(II) ion



$Pt(NH_3)_2Cl_2$ ***cis*-diamminedichloroplatinum(II)**

NH_3 as a ligand is ammine

Most metals in this section octahedral, some tetrahedral/square planar (Cu, Pt)

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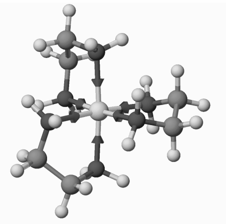
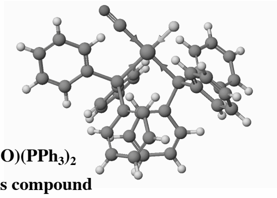
Nomenclature



Tris(ethylenediamine)nickel(II) ion

$[Ni(NH_2C_2H_4NH_2)_3]^{2+}$



$IrCl(CO)(PPh_3)_2$

Vaska's compound

Carbonylchlorobis(triphenylphosphine)iridium(I)

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Nomenclature: IUPAC Rules

$[CoCl(NH_3)_5]Cl_2$

pentaamminechlorocobalt(III) chloride

$K_2[Cd(CN)_4]$

Potassium tetracyanocadmate(II)

$NiCl_2(en)_2$

Dichlorobis(ethylenediamine)nickel(II)

$CrCl_3(C_4H_8O)_3$ *(C_4H_8O = tetrahydrofuran)*

Trichlorotris(tetrahydrofuran)chromium(III)

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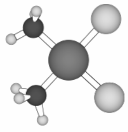
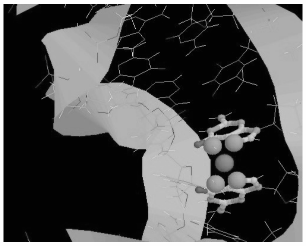
Cisplatin

cis-$[PtCl_2(NH_3)_2]$





square planar Pt(II)

coordination number 4

cis-isomer

the first of a series of platinum coordination complex-based anti-cancer drugs (Platinol-AQ)

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Isomerism

Isomers are compounds that have the same composition but a different arrangement of atoms in space

Important in inorganic *and* organic chemistry

Major Types include:

- coordination sphere isomers
- linkage isomers
- geometric isomers (*cis, trans, mer, fac*)
- stereoisomers

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Coordination Sphere Isomers

Coordination sphere isomers differ if a ligand is bonded to the metal in the *complex*, as opposed to being outside the coordination sphere (*ionic bonding*). Different reactivities!

Consider $[Co(NH_3)_5Cl]Br$ vs. $[Co(NH_3)_5Br]Cl$

$[Co(NH_3)_5Cl]Br \rightarrow [Co(NH_3)_5Cl]^+ + Br^-$

$[Co(NH_3)_5Br]Cl \rightarrow [Co(NH_3)_5Br]^+ + Cl^-$

With $AgNO_3$:

$[Co(NH_3)_5Cl]Br(aq) + AgNO_3(aq) \rightarrow [Co(NH_3)_5Cl]NO_3(aq) + AgBr(s)$

$[Co(NH_3)_5Br]Cl(aq) + AgNO_3(aq) \rightarrow [Co(NH_3)_5Br]NO_3(aq) + AgCl(s)$

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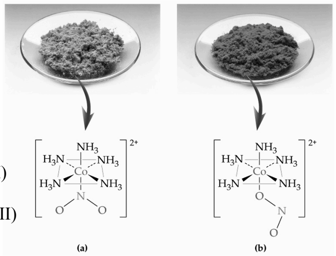
Linkage Isomers

Linkage isomers differ in which atom of a ligand is bonded to the metal in the complex

Consider $[Co(NH_3)_5(ONO)]^{2+}$ and $[Co(NH_3)_5(NO_2)]^{2+}$



a: pentaamminenitrocobalt(III) (yellow color)
b: pentaamminenitritocobalt(III) (red color)

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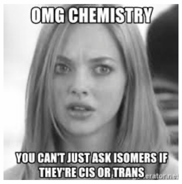
Geometric Isomers

Geometric isomers have same types and number of atoms, but they differ in the spatial arrangements of the ligands

Inorganic complexes exhibit *cis* and *trans* isomerism in square planar and octahedral complexes, as well as *mer* and *fac* isomers in octahedral complexes

Geometric isomers lead to different colors, melting points, boiling points, reactivities, solubilities, etc.



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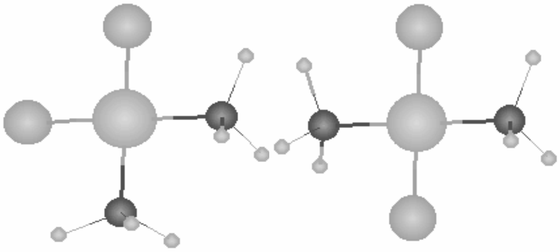
Geometric Isomers



cis isomer   trans isomer

$Pt(NH_3)_2Cl_2$ - *square planar*

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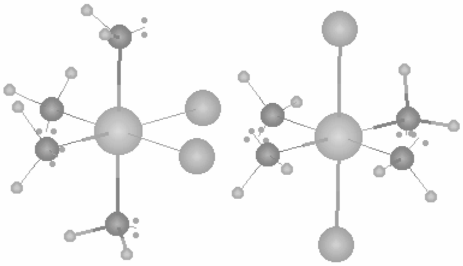
Geometric Isomers



cis isomer   trans isomer

$[Co(H_2O)_4Cl_2]^+$ - *octahedral*

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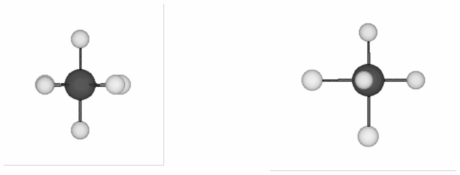
Geometric Isomers



mer isomer

fac isomer

$[CrCl_3(H_2O)_3]$ - *octahedral*

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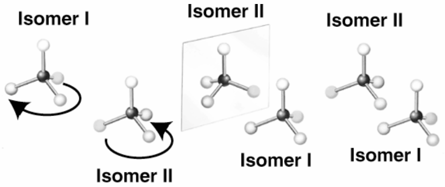
Optical Isomers

Optical isomers are isomers that are nonsuperimposable mirror images

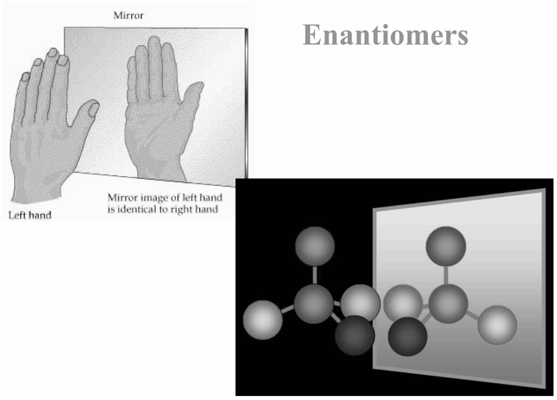
Optical isomers are called **chiral** (*handed*) and referred to as **enantiomers**

A substance is chiral if it does not have a *plane of symmetry*



MAR

Enantiomers



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Properties of Optical Isomers

Optical isomers or enantiomers possess many identical properties

Enantiomers have similar solubilities, melting points, boiling points, colors, chemical reactivity (with nonchiral reagents)

Enantiomers differ in their interactions with plane polarized light and other chiral reagents

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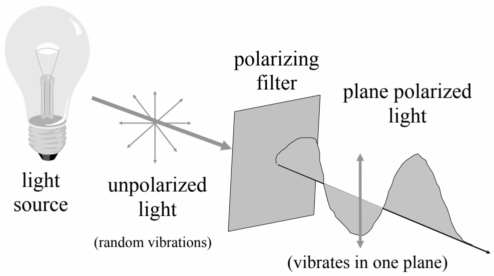
Optical Isomers



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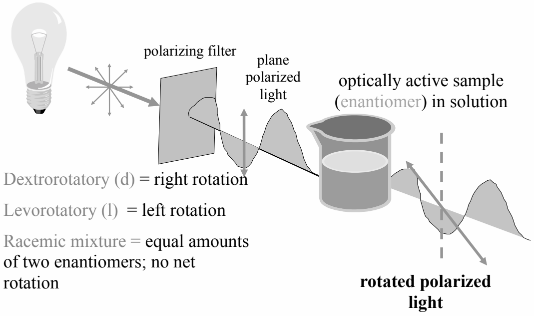
Optical Isomers



Dextrorotatory (d) = right rotation

Levorotatory (l) = left rotation

Racemic mixture = equal amounts of two enantiomers; no net rotation

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Properties of Optical Isomers

Differences in enantiomer reactivity with other chiral reagents can lead to separation methods

Example:

d-$C_4H_4O_6^{2-}(aq)$ + d,l-$[Co(en)_3]Cl_3(aq)$ →

chiral reagent *racemic mixture*

d-$[Co(en)_3](d$-$C_4H_4O_6^{2-})Cl(s)$ +

solid *d* enantiomer

l-$[Co(en)_3]Cl_3(aq) + 2Cl^-(aq)$

aqueous *l* enantiomer

Very complex procedures, but important (Ritalin, Thalidomide, etc.)

MAR

Crystal Field Theory

Crystal Field Theory is a model for bonding in transition metal complexes

Accounts for color and magnetism of complexes quite well

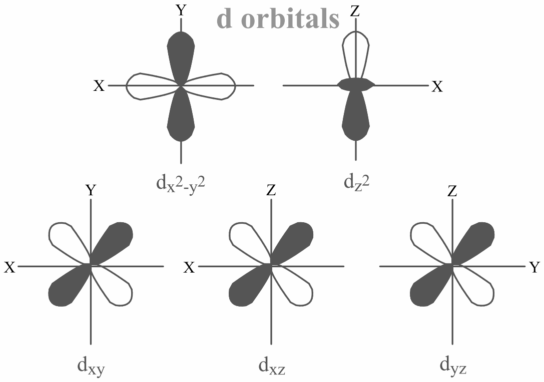
Focuses on d-orbitals of metals. Ligands are considered to be point negative charges

Assumes ionic bonding (no covalent bonding)

As in organic chemistry, ***molecular orbital theory*** *is better but much more complex*

MAR

d orbitals



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Crystal Field Theory

Electrostatic attractions between the positive metal ion and the negative ligands bond them together, *lowering* the energy of the whole system

The lone pair e^-'s on ligands repulsed by e^-'s in metal d orbitals; this interaction is called the **crystal field**

The repulsion influences d orbital energies, but not all d orbitals influenced the same way

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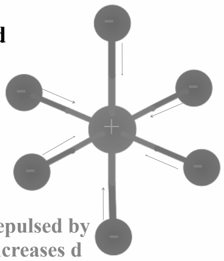
Crystal Field Theory

Octahedral Crystal Field

(-) Ligands attracted to (+) metal ion; provides stability



d orbital e^-'s repulsed by (–) ligands; increases d orbital potential energy

ligands approach along x, y, z axes

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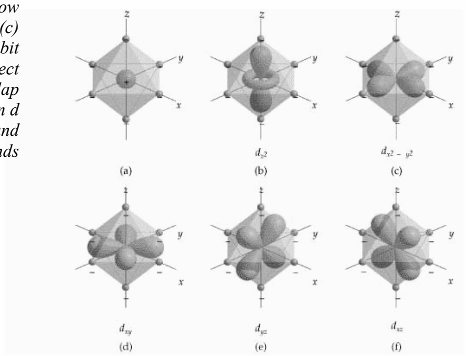
Notice how (b) and (c) exhibit direct overlap between d orbitals and ligands



d Orbitals and the Ligand Field

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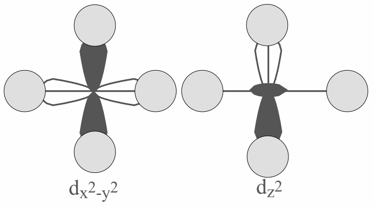
Crystal Field Theory



Lobes directed *at* ligands

greater electrostatic repulsion = higher potential energy

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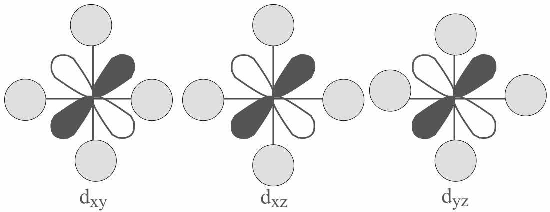
Crystal Field Theory



Lobes directed *between* ligands

less electrostatic repulsion = lower potential energy

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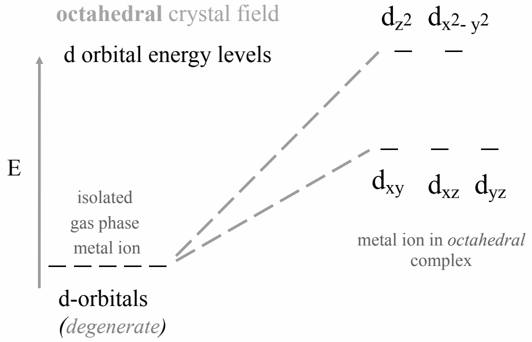
Crystal Field Theory

octahedral crystal field

d orbital energy levels



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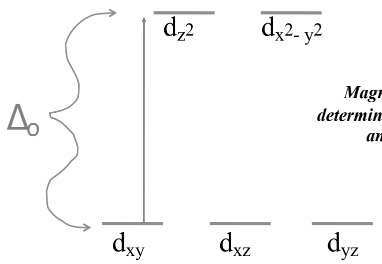
Crystal Field Splitting Energy



Magnitude of Δ_o determined by metal ion and ligand

Δ_0 **= crystal field splitting energy (J, kJ, etc.) in an octahedral (o) field**

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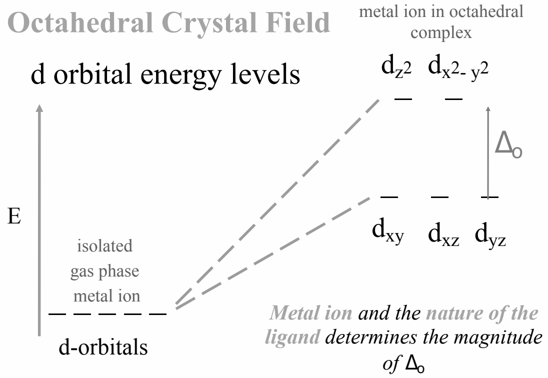
Octahedral Crystal Field

d orbital energy levels



Metal ion and the nature of the ligand determines the magnitude of Δ_o

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Crystal Field Theory

Crystal Field Theory can be used to account for the **colors** of complexes as well as **magnetic properties**

A complex *must* have a partially filled metallic d subshell to exhibit color; i.e. a complex with d^0 or d^{10} is colorless

Amount of paramagnetism depends on ligands; i.e. $[FeF_6]^{3-}$ has five unpaired electrons while $[Fe(CN)_6]^{3-}$ has only one

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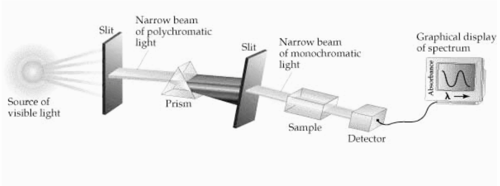
Visible Spectrum



Compounds/complexes with color ***absorb*** specific wavelengths of visible light (**400 –700 nm**); wavelengths not absorbed are ***transmitted***

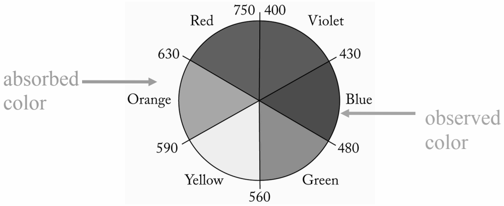
Visible Spectrum

wavelength, nm

(Each wavelength corresponds to a different color)

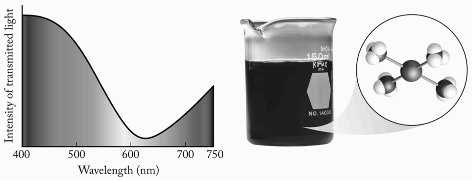
☐ White = all the colors (wavelengths)

More on Colors



The color observed in a compound/complex is actually the ***complementary*** color of the color absorbed

More on Colors



$[Cu(NH_3)_4]^{2+}$:

absorbs yellow, orange, and red…

...so observed color of complex is navy blue.

The color observed in a compound/complex is actually the ***complementary*** color of the color absorbed

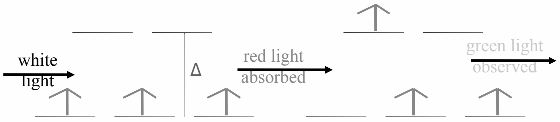
Colors of Transition Metal Complexes

Absorption of UV-visible radiation by compound or complex occurs *only* if the radiation has the energy needed to raise an e^- from its ground state (highest occupied orbital or HOMO) to an excited state (usually the lowest unoccupied orbital or LUMO)

The light energy *absorbed* = energy difference between the ground state and excited state, or

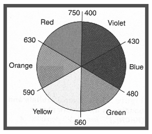
$$\Delta E = E_{LUMO} - E_{HOMO} = h\nu = hc/\lambda_{max}$$

Colors of Transition Metal Complexes



For transition metal complexes, Δ corresponds to energies of visible light.

Absorption raises an electron from the lower d subshell to the higher d subshell.



Colors of Transition Metal Complexes

The **magnitude** of Δ depends on the **ligand field** (i.e. *types of ligands*) and the **metal**, and Δ determines the **color** of the complex

Different complexes exhibit different colors due to the magnitude of Δ

larger Δ = higher energy light absorbed, shorter wavelengths

smaller Δ = lower energy light absorbed, longer wavelengths

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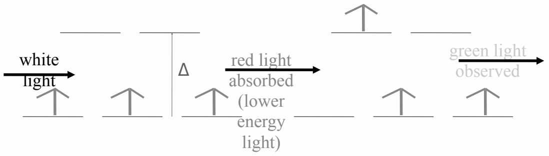
Colors of Transition Metal Complexes



white light

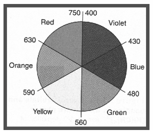
Δ

red light absorbed (lower energy light)

green light observed

$[Cr(H_2O)_6]^{3+}$

H_2O is a "weak field ligand"



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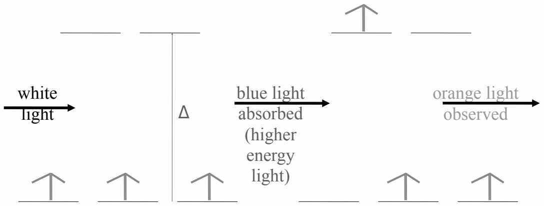
Colors of Transition Metal Complexes



white light

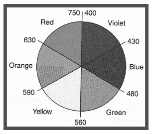
Δ

blue light absorbed (higher energy light)

orange light observed

$[Cr(en)_3]^{3+}$

en is a "strong field ligand"



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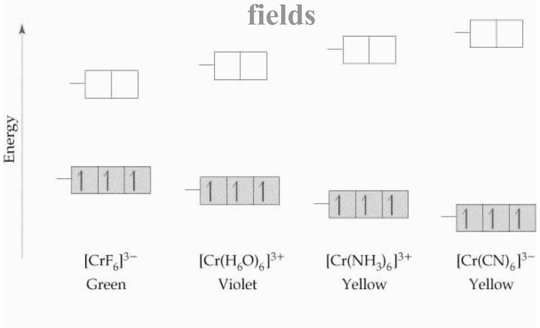
Chromium(III) with different ligand fields



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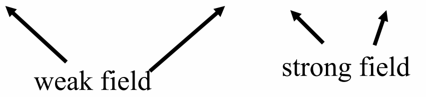
Colors of Transition Metal Complexes

The Spectrochemical Series:

Smallest Δ — Δ increases — Largest Δ

$I^- < Br^- < Cl^- < OH^- < F^- < H_2O < NH_3 < en < O_2 < CN^- < CO$



weak field

strong field

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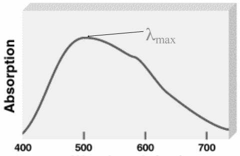
Spectrochemical Series



Examples with chromium(III):

Complex	λ_{max} (nm)	
$CrCl_6^{3-}$	736	*largest λ_{max}, smallest Δ*
$Cr(H_2O)_6^{3+}$	573	
$Cr(NH_3)_6^{3+}$	462	
$Cr(CN^-)_6^{3-}$	380	*smallest λ_{max}, largest Δ*

$I^- < Br^- < Cl^- < OH^- < F^- < H_2O < NH_3 < en < O_2 < CN^- < CO$

Smallest Δ — Δ increases — Largest Δ

MAR

Paramagnetism of Transition Metal Complexes

Many complexes / compounds are paramagnetic due to unpaired d electrons

The degree of paramagnetism dependent on ligands ("ligand field")

Example with Fe^{3+}:

[Fe(CN)$_6$]$^{3-}$ has 1 unpaired d electron

[FeF$_6$]$^{3-}$ has 5 unpaired d electrons

Crystal Field Theory answers this discrepancy

MAR

Electronic Configurations of Transition Metal Complexes

Filling electron shells via CH 221:

- lowest energy vacant orbitals are occupied first
- electrons fill degenerate orbitals singly until no longer possible (Hund's rule), then pair (Pauli Exclusion)

These rules help minimize repulsions between electrons.

These rules work well for *gas-phase transition metal ions*, but they are not always followed by *transition metal complexes in a ligand field*

MAR

Electronic Configurations of Transition Metal Complexes

For complexes in a ligand field, d orbital occupancy depends on Δ and *pairing energy*, P

- Electrons assume the configuration with the lowest possible energy "cost"
- If $\Delta > P$ (Δ large; strong field ligand), e$^-$'s pair up in **lower energy d subshell first**, referred to as a **low spin** complex
- If $\Delta < P$ (Δ small; weak field ligand), e$^-$'s **spread out among all d orbitals** before any pair up, referred to as a **high spin complex**

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d-orbital energy level diagrams octahedral complex

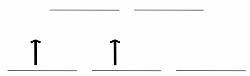
d^1

one unpaired electron

MAR

d-orbital energy level diagrams octahedral complex

d^2



two unpaired electrons

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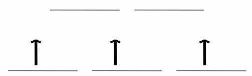
d-orbital energy level diagrams octahedral complex

d^3



three unpaired electrons

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d-orbital energy level diagrams octahedral complex

d^4

high spin

$\Delta < P$

four unpaired electrons

low spin

$\Delta > P$

two unpaired electrons

MAR

d-orbital energy level diagrams octahedral complex

d^5

high spin

$\Delta < P$

five unpaired electrons

low spin

$\Delta > P$

one unpaired electron

MAR

d-orbital energy level diagrams octahedral complex

d^6

high spin

$\Delta < P$

four unpaired electrons

low spin

$\Delta > P$

no unpaired electrons

MAR

d-orbital energy level diagrams octahedral complex

d^7

high spin

$\Delta < P$

three unpaired electrons

low spin

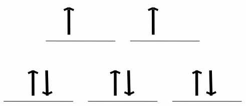
$\Delta > P$

one unpaired electron

MAR

d-orbital energy level diagrams octahedral complex

d^8

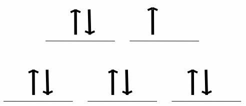


two unpaired electrons

MAR

d-orbital energy level diagrams octahedral complex

d^9

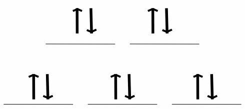


one unpaired electron

MAR

d-orbital energy level diagrams octahedral complex

d^{10}



no unpaired electrons
diamagnetic
colorless

MAR

Electronic Configurations of Transition Metal Complexes

To determine which d-orbital energy level diagram to use on a complex or compound:

- determine the oxidation # of the metal
- determine the # of d e$^-$'s
- determine if ligand is weak field or strong field
- draw energy level diagram

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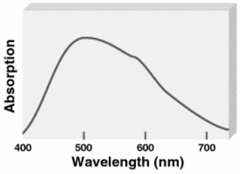
Example with $Co(NH_3)_6^{3+}$

The absorbance spectrum of $Co(NH_3)_6^{3+}$ is shown to the right.



1. What is the name of the complex?
2. What is the coordination number?
3. How many d electrons does the complex possess?
4. Will this be a high spin or low spin complex?
5. Is the compound paramagnetic?
6. What is the value of Δ for this complex?
7. What will be the observed color of the complex? What color is absorbed?

MAR

Example with $Co(NH_3)_6^{3+}$

1. What is the name of the complex?

   Each ammonia is neutral; hence, this is a cobalt(III) complex

   Ammonia is named "ammine"; hence,

   Name = **hexaamminecobalt(III) ion**

2. What is the coordination number?

   There are six monodentate ammonia ligands around the cobalt(III) ion; hence, this is a six coordinate compound, or the **coordination number = 6**

MAR

Example with $Co(NH_3)_6^{3+}$

3. How many d electrons does the complex possess?

   Cobalt(III) ions have the electron configuration:

   $[Ar]3d^6$ *(two 4s and 1 3d electron removed)*

   This complex has **six d electrons** (**d^6**)

4. Will this be a high spin or low spin complex?

   To answer this, we need to look at the spectrochemical series.

   NH_3 is considered a strong field ligand, which implies that Δ, the splitting energy, will be greater than the electron pairing energy (P).

   The octahedral NH_3 ligand field makes this a **low spin complex**

MAR

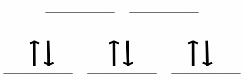
Example with $Co(NH_3)_6^{3+}$

5. Is the compound paramagnetic?

   This is a d^6 low spin complex in an octahedral field.

   Three degenerate d orbitals are filled first, followed by the remaining two orbitals.

   Since each orbital holds two electrons, the three lower orbitals are full and the complex is **diamagnetic**



low spin

$\Delta > P$

no unpaired electrons

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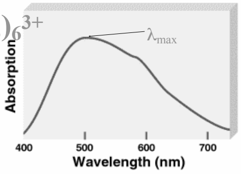
Example with $Co(NH_3)_6{}^{3+}$

The absorbance spectrum of $Co(NH_3)_6{}^{3+}$ is shown to the right.



6. What is the value of Δ for this complex?

Notice that $\lambda_{max} = 500.$ nm in the spectrum, and technically this is a question asking for Δ since the complex is in an octahedral field

$\Delta_O = \Delta E = h\nu = hc/\lambda_{max}$

$\Delta_O = 6.626*10^{-34}$ J s $*$ $2.998*10^{8}$ m s^{-1} / $500.*10^{-9}$ m

$\Delta_O = 3.97*10^{-19}$ J *or*

$\Delta_O = 239$ kJ/mol

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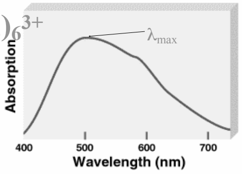
Example with $Co(NH_3)_6{}^{3+}$

The absorbance spectrum of $Co(NH_3)_6{}^{3+}$ is shown to the right.

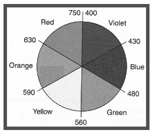


7. What will be the observed color of the complex? What color is absorbed?

Since λ_{max} is 500. nm in the spectrum, this is the wavelength that is absorbed.

Using 500. nm, the chart to the right implies that the complex is absorbing the color green

The complementary color is the color that is actually observed by our eyes. Red is opposite green, so the observed color should be red



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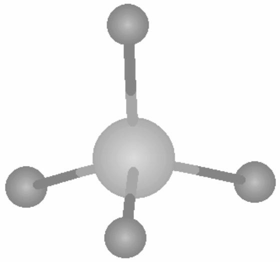
d-orbital energy level diagrams for tetrahedral complexes



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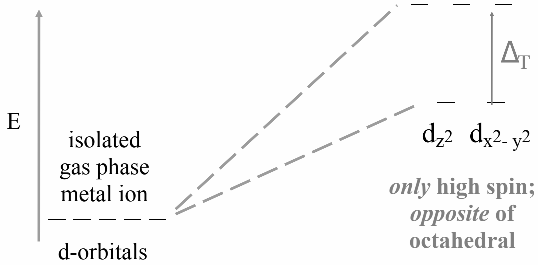
d-orbital energy level diagram for tetrahedral complexes



metal ion in tetrahedral complex

d_{xy} d_{xz} d_{yz}

Δ_T

d_{z^2} $d_{x^2-y^2}$

E

isolated gas phase metal ion

d-orbitals

***only* high spin; *opposite* of octahedral**

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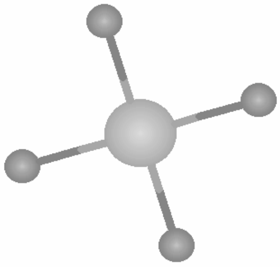
d-orbital energy level diagrams for square planar complexes



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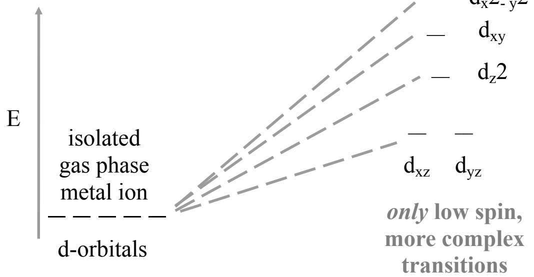
d-orbital energy level diagram for square planar complexes



metal ion in square planar complex

$d_{x^2-y^2}$

d_{xy}

d_{z^2}

d_{xz} d_{yz}

E

isolated gas phase metal ion

d-orbitals

***only* low spin, more complex transitions**

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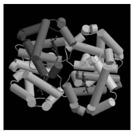
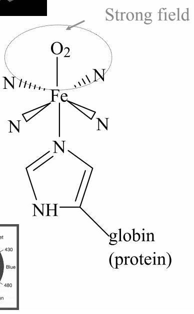
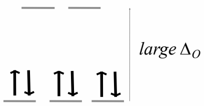


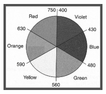
Example: Arterial Blood

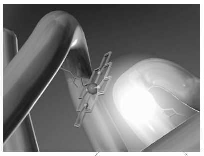




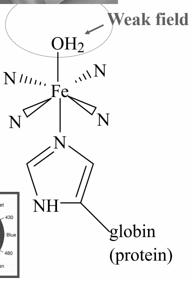
d^6, low spin

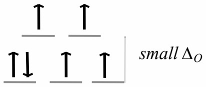
Bright red due to absorption of greenish light





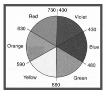
Example: Venous Blood

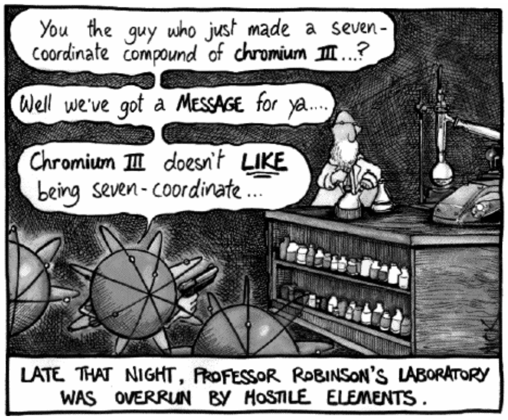




d^6, high spin

Bluish color due to absorption of orange light

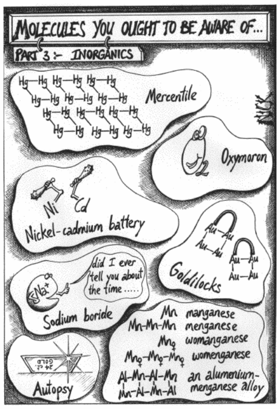




End of Chapter 19

See:

- ✳ Chapter Nineteen Study Guide
- ✳ Important Equations (following this slide)
- ✳ End of Chapter Problems (following this slide)



Important Equations, Constants, and Handouts from this Chapter:

- **The primary focus of this chapter is to introduce you to coordination compound nomenclature (with a little review of metals, electron configurations, etc. as well from CH 221 and CH 222)**

Handouts:

- *Coordination Compounds Handout*

End of Chapter Problems: ***Test Yourself***

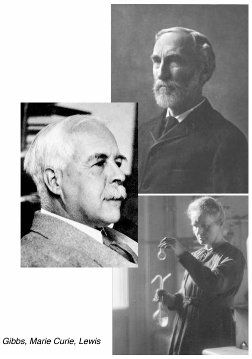
1. Give the electron configuration for the Cr^{3+} ion. Is it paramagnetic or diamagnetic?
2. Which of the following ligands is expected to be monodentate and which might be polydentate? a. CH_3NH_2 b. CH_3CN c. en d. Br^{-1} e. phen
3. Give the oxidation number of the metal ion in $[Mn(NH_3)_6]SO_4$
4. Give the oxidation number of the metal ion in $Cr(en)_2Cl_2$
5. Write the formula for potassium tetrachloroplatinate(II)
6. Write the formula for tetraamminediaquairon(II)
7. Name the following: $[Ni(C_2O_4)_2(H_2O)_2]^{2-}$
8. Name the following: $Pt(NH_3)_2(C_2O_4)$

End of Chapter Problems: *Answers*

1. [Ar]3d^3, paramagnetic
2. a, b, d: monodentate c, e: polydentate (bidentate)
3. +2
4. +2
5. $K_2[PtCl_4]$
6. $[Fe(NH_3)_4(H_2O)_2]^{2+}$
7. diaquabis(oxalato)nickelate(II) ion
8. diammineoxalatoplatinum(II)

MAR

Chemistry 223 Final Exam Review



Clockwise from top: Gibbs, Marie Curie, Lewis

Chemistry 223
Professor Michael Russell

Last update:
4/29/24

MAR

Which statement describes the composition of a neutral atom of iron-58?

A. 26 neutrons, 32 protons, and 26 electrons
B. 32 neutrons, 26 protons, and 26 electrons
C. 26 neutrons, 26 protons, and 32 electrons
D. 26 neutrons, 26 protons, and 26 electrons
E. Not enough information

MAR

Nitrogen and oxygen form a series of oxides with the general formula N_xO_y. One of them has 46.67% N. The empirical formula for this oxide is

A. N_2O
B. NO
C. NO_2
D. N_2O_3
E. N_2O_5

MAR

Ammonia is prepared by the reaction:

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

If 10.0 mol of N_2 are mixed with 25.0 mol of H_2, the amount of NH_3 produced will be:

A. 20.0 mol NH_3
B. 16.7 mol NH_3
C. 37.5 mol NH_3
D. 25.0 mol NH_3
E. 35.0 mol NH_3

MAR

Which of the compounds below would be the best conductor of electricity in aqueous solution?

A. CH_3CO_2H
B. H_3PO_4
C. NH_3
D. HBr
E. HIO

MAR

Which equation below best represents the balanced net ionic equation for the reaction of potassium hydroxide and iron(II) chloride to give iron(II) hydroxide and potassium chloride?

A. $2\ KOH(aq) + FeCl_2(aq) \rightarrow Fe(OH)_2(s) + 2\ KCl(aq)$
B. $2\ KOH(aq) + FeCl_2\ (aq) \rightarrow Fe(OH)_2(aq) + 2\ KCl(aq)$
C. $2\ OH^–(aq) + Fe^{2+}(aq) \rightarrow Fe(OH)_2(s)$
D. $K^+(aq) + Cl^–(aq) \rightarrow KCl(aq)$

MAR

Assume you dissolve 6.73 g Na_2CO_3 in enough water to make 250. mL of solution. (Molar mass of Na_2CO_3 = 106 g/mol.) What is the concentration of the sodium carbonate?

A. 26.9 M
B. 0.0635 M
C. 0.254 M
D. 0.762 M
E. 42 M

MAR

What is the oxidation number for Mn in $KMnO_4$?

A. 0
B. +2
C. +4
D. +7
E. +8

MAR

Calculate the enthalpy for the reaction

$$SiH_4(g) + 2\ O_2(g) \rightarrow SiO_2(g) + 2\ H_2O(g)$$

using these values:
$\Delta H^\circ_f[SiH_4(g)]$ = +34.3 kJ/mol;
$\Delta H^\circ_f[SiO_2(g)]$ = -910.9 kJ/mol; and
$\Delta H^\circ_f[H_2O(g)]$ = -241.8 kJ/mol

A. -1187.0 kJ/rxn
B. -1428.8 kJ/rxn
C. -1360.2 kJ/rxn
D. -2218.7 kJ/rxn
E. Not enough information

MAR

The correct general valence electronic configuration for the alkali metals is:

A. ns^1
B. ns^2
C. $ns^2\ np^1$
D. $ns^2\ np^5$
E. $ns^2\ np^6$

MAR

Compare the elements Na, B, Al, and C with regard to the following properties:
Which has the largest atomic radius?

A. Na
B. B
C. Al
D. C
E. Jq

MAR

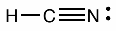
Compare the elements K, B, Al, and N with regard to the following properties:
Which has the largest electronegativity?

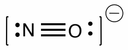
A. K
B. B
C. Al
D. N
E. Jq

MAR

Which of the following is NOT a correct Lewis dot structure?

A. 

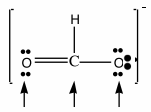
C. 

B. 

D. 

MAR

Determine the formal charges for the formate ion:

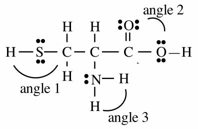


Formal charge = ____ ____ ____

A. 0 0 0
B. +1 –1 –1
C. +1 0 –1
D. 0 0 –1

MAR

Cysteine is one of the natural amino acids.



Estimate the values of the indicated angles:

A. Angle 1 = 180˚ Angle 2 = 120˚ Angle 3 = 109˚
B. Angle 1 = 109˚ Angle 2 = 120˚ Angle 3 = 109˚
C. Angle 1 = 109˚ Angle 2 = 109˚ Angle 3 = 109˚

MAR

Which of the following could be an alkene?

A. $C_nH_{2n+2}O$
B. C_nH_{2n+2}
C. C_nH_{2n}
D. C_nH_{2n-2}
E. none of these

MAR

A sample of gas has a volume of 222 mL at 695 mm Hg and 0 °C. What would be the volume of this same sample of gas if it were measured at 333 mm Hg and 0 °C?

A. 894 mL
B. 463 mL
C. 657 mL
D. 359 mL
E. -155 mL

MAR

Gas density: Which has the greatest density at 25 °C and 1.00 atm pressure?

A. O_2
B. N_2
C. H_2
D. CO_2
E. Xe

MAR

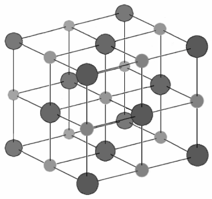
Under what conditions will the ideal gas law be least effective?

A. high temperature and high pressure
B. high temperature and low pressure
C. low temperature and high pressure
D. low temperature and low pressure
E. it works all the time

MAR

In the diagram for NaCl, the smaller blue atoms are Na and the larger green atoms are Cl. How many nearest neighbors of Cl does each Na have?

A. 8
B. 6
C. 4
D. 2
E. 1



MAR

Which water-based solution is expected to have the higher boiling point?

A. 0.10 molal NaCl
B. 0.15 molal sugar
C. both the same
D. not enough information

MAR

Erythritol occurs naturally in algae and fungi. A solution of 2.50 g of erythritol in 50.0 g of water freezes at -0.762 °C. What is the molar mass of the compound? ($k_{fp}(H_2O)$ = -1.86 °C/m)

A. 26.9 g/mol
B. 35.5 g/mol
C. 122 g/mol
D. 224 g/mol
E. 0.0100 g/mol

MAR

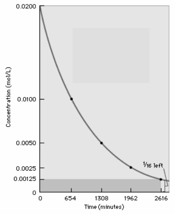
Given the initial rate data for the reaction A + B → C, determine the rate expression for the reaction.

[A] (M)	[B] (M)	Δ[C]/Δt (M/s)
0.10	0.20	40.
0.20	0.20	80.
0.10	0.10	40.

A. $\Delta[C]/\Delta t = 2000[A][B]$
B. $\Delta[C]/\Delta t = 40.[A]^2$
C. $\Delta[C]/\Delta t = 4.0[B]$
D. $\Delta[C]/\Delta t = 400[A]$
E. Δ[C]/Δt = #1[AC/DC]

MAR

Using the graph, determine the half life of this reaction.



A. 654 minutes
B. 1308 minutes
C. 1962 minutes
D. 2616 minutes
E. 0 minutes

MAR

Radioactive iodine-131 is used to treat hyperthyroidism. It has a half-life of 8.04 days. If you begin with 8.8 micrograms, what mass remains after 32.3 days?

A. 4.4 micrograms
B. 2.2 micrograms
C. 1.1 micrograms
D. 0.54 micrograms
E. 0.23 micrograms

The reaction of $NO_2(g)$ and $CO(g)$ is thought to occur in two steps.

Step 1 Slow	$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$
Step 2 Fast	$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

Which species is acting as a catalyst in this mechanism?

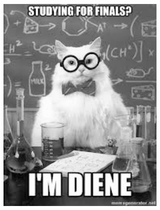
A. NO_2
B. NO
C. CO
D. CO_2
E. NO_3

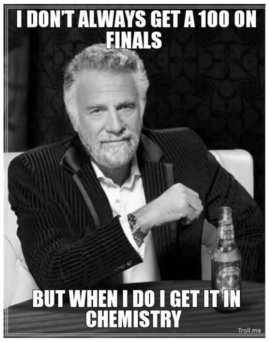
What is the unknown particle in the following nuclear reaction?

$^{239}_{92}U \rightarrow \text{particle} + {}^{239}_{93}Np$

A. alpha
B. beta
C. gamma
D. neutron
E. positron

End of Review - *good luck with your studying!*





Need more practice?

- *Practice Problem Sets (online)*
- *Concept Guides (Companion and online)*
- *Chapter Guides (online)*
- *End of Chapter Problems in Textbook (every other question has answer at end)*

Good luck with your studying!

Types of Equilibrium Constants in CH 223

K_a Acid Dissociation Constant (Chapter 14)

For the reaction: $HA + H_2O <=> H_3O^+ + A^-$,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

K_b Base Dissociation Constant (Chapter 14)

For the reaction: $B^- + H_2O <=> OH^- + HB$,

$$K_b = \frac{[OH^-][HB]}{[B^-]}$$

K_c Equilibrium Constant using Molarity (Chapter 13)

For the reaction: $a\,A + b\,B <=> c\,C + d\,D$,

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K_f Formation Constant (Chapter 14 and 15)

For the reaction: $M^{2+} + 4\,L_{(aq)} <=> ML_4^{2+}$,

$$K_f = \frac{[ML_4^{2+}]}{[M^{2+}][L]^4}$$

K_p Equilibrium Constant using Pressure (atm) (Chapter 13)

For the reaction: $\frac{1}{2} N_{2(g)} + O_{2(g)} <=> NO_{2(g)}$,

$$K_p = \frac{P_{NO_2}}{P_{N_2}^{0.5} P_{O_2}}$$

Also: $K_p = K_c(RT)^{\Delta n}$

K_{sp} Solubility Product Constant (Chapter 15).
For the reaction: $ML_{2(S)} \Leftrightarrow M^{2+} + 2\,L^-$,

$$K_{sp} = \left[M^{2+}\right]\left[L^-\right]^2$$

K_{spa} Solubility Product Constant in Acid (Chapter 15)
For the reaction: $ZnS_{(s)} + 2\,H_3O^+ \Leftrightarrow Zn^{2+} + H_2S + 2\,H_2O_{(l)}$,

$$K_{spa} = \frac{\left[Zn^{2+}\right]\left[H_2S\right]}{\left[H_3O^+\right]^2}$$

K_w Autoionization of Water Constant (Chapter 14)
For the reaction: $2\,H_2O_{(l)} \Leftrightarrow H_3O^+ + OH^-$,

$$K_w = \left[H_3O^+\right]\left[OH^-\right] = 1.00 * 10^{-14} \text{ at } 25\ ^\circ\text{C}$$

k Kinetics Rate Constant (Chapter 12). The forward reaction (k_1) and the reverse reaction (k_{-1}) are related to the equilibrium constant, **K**, by

$$K = \frac{k_1}{k_{-1}}$$

Q Reaction Quotient (Chapter 13, 15, and 17), for non-equilibrium calculations. Q is defined in a method similar to that of K.

Understanding K and Q in CH 223

For the reaction: **$a\,A_{(aq)} + b\,B_{(aq)} <=> c\,C_{(aq)} + d\,D_{(aq)}$**,
the **equilibrium constant, K,** is defined as:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

If K >> 1, the reaction is product favored

Equilibrium concentrations of products are greater than the equilibrium concentrations of reactants

If K << 1, the reaction is reactant favored

Equilibrium concentrations of reactants are greater than the equilibrium concentrations of products

If K = 1, the concentration of products equals the concentration of reactants

This condition is extremely rare and will not be seen in CH 223.

The **Reaction Quotient, Q,** is used to compare experimental conditions to equilibrium positions.
Q is a <u>**ratio of concentrations**</u> similar to the definition of **K**, above.
The concentrations for **K** should be at equilibrium, while the concentrations given for **Q** *may not* be at equilibrium.

- **If Q > K, the reaction is not at equilibrium,** and the reaction will move to the **reactants**.
- **If Q < K, the reaction is not at equilibrium,** and the reaction will move to the **products**.
- **If Q = K, the reaction is at equilibrium**

Manipulating Equilibrium Constant Expressions

Remember, for the reaction: **a $A_{(aq)}$ + b $B_{(aq)}$ <=> c $C_{(aq)}$ + d $D_{(aq)}$,**

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Products in numerator, reactants in denominator
- Raise the stoichiometric value to the same factor for each species present
- Only gases and dissolved species appear in equilibrium constant expressions
- Solids and liquids do not appear in equilibrium constant expressions
- Remember to watch for units!

1. *Do not include solids and liquids in equilibrium calculations, only gases and dissolved species*
Example 1: **$C_{(s)}$ + $^1/_2$ $O_{2(aq)}$ <=> $CO_{(aq)}$**

$$K_1 = \frac{[CO]}{[O_2]^{1/2}} = 4.6*10^{23}\ M^{1/2} \text{ at } 25\ ^\circ C$$

2. *If doubling reaction, square K; if tripling, cube K; etc.*
Example 2: **2 $C_{(s)}$ + $O_{2(aq)}$ <=> 2 $CO_{(aq)}$**

$$K_2 = \frac{[CO]^2}{[O_2]} = (K_1)^2 = (4.6*10^{23})^2 = 2.1*10^{47}\ M \text{ at } 25\ ^\circ C$$

Also, if reaction*3, $K = (K_1)^3$; if reaction halved, $K = (K_1)^{1/2}$; *etc.*

3. *If reactants and products are "flipped", take 1/K for new value..*
Example 3: **$CO_{(aq)}$ <=> $C_{(s)}$ + $^1/_2$ $O_{2(aq)}$**

$$K_3 = \frac{[O_2]^{1/2}}{[CO]} = \frac{1}{K_1} = \frac{1}{4.6*10^{23}} = 2.2*10^{-24}\ M^{-1/2} \text{ at } 25\ ^\circ C$$

4. *Temperature changes will affect the value of K by either adding or subtracting from the original value.*

Example 4: $\mathbf{C_{(s)} + {}^{1}/_{2}\,O_{2(aq)} <\!=\!> CO_{(aq)}}$

$$K_4 = \frac{[CO]}{[O_2]^{1/2}} = \mathbf{9.7*10^{23}\ M^{1/2}\ at\ 37\ ^{\circ}C}$$

5. *Reactions in the gas phase use K_p expressions which are similar to K_c expressions*

Example 5: $\mathbf{C_{(s)} + {}^{1}/_{2}\,O_{2(g)} <\!=\!> CO_{(g)}}$

$$K_5 = \frac{P_{CO}}{P_{O_2}^{1/2}} = K_p, \quad \textit{and if at 25 °C (298 K),}$$

$$K_p = K_c(RT)^{\Delta n} = 4.6*10^{23}(0.082057*298)^{1-1/2} = \mathbf{2.3*10^{24}\ atm^{1/2}}$$

R = gas constant, T = Kelvin temperature, P in atm

6. *If adding reactions, multiply the respective K values together*

Example 6: $\mathbf{C_{(s)} + {}^{1}/_{2}\,O_{2(aq)} <\!=\!> \cancel{CO_{(aq)}}}$ $\quad\mathbf{K_1 = 4.6*10^{23}\ M^{1/2}}$

$\mathbf{\cancel{CO_{(aq)}} + {}^{1}/_{2}\,O_{2(aq)} <\!=\!> CO_{2(aq)}}$ $\quad\mathbf{K_6 = 1.7*10^{15}\ M^{-1/2}}$

----

net reaction: $\mathbf{C_{(s)} + O_{2(aq)} <\!=\!> CO_{2(aq)}}$ $\quad\mathbf{K_7}$

Assume at 25 °C:

$$K_7 = K_1*K_6 = \frac{[CO]}{[O_2]^{1/2}} * \frac{[CO_2]}{[CO][O_2]^{1/2}} = (4.6*10^{23})(1.7*10^{15}) = \mathbf{7.8*10^{38}}\ \textit{unitless}$$

CH 223 Guide to Le Chatelier's Principle

Le Chatelier's Principle: "If a stress is applied to a system, the system will change in a manner to reduce the stress"

Disturbance	**Change as Mixture Returns to Equilibrium**	**Effect on Equilibrium**	**Effect on K**
Addition of Reactant	Some of added reactant is consumed	Shift to **right** (products)	*No change*
Addition of Product	Some of added product is consumed	Shift to **left** (reactants)	*No change*
Decrease in Volume, Increase in Pressure, Addition of Inert Gas	Pressure increases	Shift toward **fewer gas molecules**	*No change*
Increase in Volume, Decrease in Pressure	Pressure decreases	Shift toward **more gas molecules**	*No change*
Rise in Temperature	Heat energy is consumed	Shift in the **endothermic** direction	**Change**
Drop in Temperature	Heat energy is generated	Shift in the **exothermic** direction	**Change**

Example: For $PbCl_{2(s)}$ **<=>** $Pb^{2+}_{(aq)} + 2\ Cl^{-1}_{(aq)}$, $K_{sp} = 1.7 * 10^{-5}$. If $Pb^{2+}_{(aq)}$ is added to the system at equilibrium, some of the added product will be consumed (Pb^{2+} and Cl^{-1}), and the reaction will shift to the left. The value of K_{sp} remains constant at $1.7 * 10^{-5}$.

Example: For $N_{2(g)} + O_{2(g)} \ {<=>}\ 2\ NO_{(g)}$, $\Delta H° = +180.5$ kJ and $K = 4.5 * 10^{-31}$ at **298 K**. If the temperature is raised to **900 K**, K changes to $6.7 * 10^{-10}$ - more product favored, heat energy is consumed, and the value of K has changed.

CH 223 Chapter Thirteen Study Guide

- Know the nature of equilibrium (reversible reactions, dynamic processes, etc.) Realize that while many chemical reactions are in equilibrium, many are simple "one-way" reactions as well.

- Be able to write an equilibrium constant expression for any reaction. Know how to find K_c or K_p given the appropriate information.

- Recognize that solids and liquids are not included in equilibrium constant expressions. Know how the expression can change depending on the stoichiometry of the reaction.

- Know how to convert K_c to K_p given appropriate information.

- Know the difference between initial concentration and equilibrium concentration. Be able to find the equilibrium constant based on this information.

- Understand the effect on K when two chemical reactions are combined together. Know the effect on K when the reaction is reversed, or when the reaction stoichiometry is doubled.

- Know when a value of K should be "product favored" or "reactant favored".

- Realize the importance of the reaction quotient, Q, when deciding if the reaction is at equilibrium. Be able to predict the progress of the reaction based on the value of Q.

- Be able to apply Le Chatelier's principle to predict the effect of a disturbance on a chemical equilibrium (change in temperature, change in concentration, change in volume, change in pressure, effect of exothermic or endothermic reactions, etc.)

- Understand the relationship between a reaction mechanism and on the kinetics of a reaction if one step in the mechanism involves a chemical equilibrium.

- Be able to solve and understand the assigned problems in problem set #1.

Brønsted Acids and Bases

A **Brønsted Acid** will donate a proton, while a **Brønsted Base** will accept a proton

$$\underset{base}{\mathbf{NH_3}} + \underset{acid}{\mathbf{H_2O}} \Leftrightarrow \underset{acid}{\mathbf{NH_4^+}} + \underset{base}{\mathbf{OH^-}}$$

A base produces a **conjugate acid** upon acceptance of a proton

An acid produces a **conjugate base** upon release of a proton

Acids do not create conjugate acids, and bases do not create conjugate bases

Some acids and bases are **polyprotic** - more than one proton can be released or accepted.

Example: Sulfuric acid is a diprotic acid

$H_2SO_4 \rightarrow HSO_4^- + H^+$
$HSO_4^- \rightarrow SO_4^{2-} + H^+$

$\mathbf{H_2SO_4 \rightarrow SO_4^{2-} + 2\,H^+}$

Example: Magnesium hydroxide is a diprotic base

$Mg(OH)_2 \rightarrow 2\,OH^- + Mg^{2+}$
$2\,OH^- + 2\,H^+ \rightarrow 2\,H_2O$

$\mathbf{Mg(OH)_2 + 2\,H^+ \rightarrow 2\,H_2O + Mg^{2+}}$

Strong Acids and **Strong Bases** are completely ionized.
Weak Acids and **Weak Bases** have equilibrium constants, **K**, less than one. Use your textbook as a source of K values for acids and bases.

CH 223 Chapter Fourteen Part I Study Guide

- Know the three major acid-base theories discussed in the chapter.
- Be able to identify and name common strong and weak acids and bases.
- Be familiar with the Arrhenius theory of acids.
- Be able to recognize common monoprotic and polyprotic acids and bases. Know how to write balanced equations for their ionization in water.
- Know the definition of amphiprotic.
- Be able to recognize Brønsted acids and bases in reactions.
- Know the definition of conjugate and know how it applies to acids and bases.
- Know how to use values of K_a and K_b to predict the relative strengths of acids and bases
- Know how to predict when an acid-base reaction is reactant- or product-favored.
- ***MEMORIZE*** the value of K_w. the water autoionization constant.
- Be able to calculate **pH** and **pOH** for a solution. Know how to find $[H^+]$ or $[OH^-]$ from pH or pOH.
- Be able to calculate equilibrium constants using K_a, K_b, pH, pOH, etc.
- Be able to describe the acid-base properties of salts and calculate the pH of salt solutions.
- Understand the importance of the Lewis concept of acids and bases. Know what qualifies as a Lewis acid or a Lewis base.
- Be able to solve and understand the assigned problems in problem set #2.

Buffers & Henderson-Hasselbalch

<u>The three things you need to know about buffers are</u>:

1) A **buffer** consists of a weak acid with its conjugate base (or a weak base with its conjugate acid). Strong acids and bases do not form buffers.

Examples: CH_3CO_2H / CH_3CO_2Na could be a buffer system
NH_3 / NH_4Cl could be a buffer system
HCl / NaCl would not be a buffer system (strong acid)
CH_3CO_2H / NH_3 would not be a buffer system (not conjugates)

2) Although you can use the "long" method using equilibrium concentrations, etc., the **Henderson-Hasselbalch equation** will almost always be much easier to utilize.

The Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{Conj. base}]}{[\text{acid}]}$$

where pH = pH of system
$pK_a = -\log K_a = -\log$ (acid dissociation constant for weak acid in buffer)
[Conj. base] = concentration *or* moles of base in solution
[acid] = concentration *or* moles of acid in solution

For the Henderson-Hasselbalch equation to be effective, the ratio of [conj. base]/[acid] must be no larger than 10 and no less than 0.1.

Example: What is the pH of a buffer with $[CH_3CO_2H] = 0.700$ M and $[CH_3CO_2^-] = 0.600$ M? K_a for acetic acid = $1.8*10^{-5}$

$pK_a = -\log K_a = -\log(1.8*10^{-5}) = \mathbf{4.74}$
Now use the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{Conj. base}]}{[\text{acid}]} = 4.74 + \log\frac{[0.600]}{[0.700]} = \mathbf{4.67}$$

3) When selecting an appropriate buffer, choose a pK_a value which is close to the desired pH of your buffer. This maintains the appropriate Henderson-Hasselbalch ratio and makes your calculations must easier.

Example: If a buffer with a pH of 4.5 was desired, acetic acid and sodium acetate would be a good system to use. As observed in #2, pK_a for acetic acid is 4.74 - this is close to pH = 4.5, so this would be a good system.

Example: If a buffer with a pH of 4.5 was desired, potassium hydrogen phosphate and potassium phosphate would ***not*** be a good system to use. The weak acid here is potassium hydrogen phosphate; the K_a is $3.6*10^{-13}$, or $pK_a = 12.44$ - too basic for our desired acidic pH of 4.5.

Buffer Calculations upon Addition of Strong Acids or Bases

The Henderson-Hasselbalch equation can give you more than just the pH of solutions; it can also tell you what the pH of the solution will be upon addition of strong acid or strong base.

Example: As we saw earlier, the pH of a buffer with $[CH_3CO_2H] = 0.700$ M and $[CH_3CO_2^{-1}] = 0.600$ M is 4.67 ($pK_a = 4.74$) What will the pH be upon the addition of 10.00 mL of 1.00 M HCl? Assume 1.00 L of buffer before addition of HCl.

Remember that the Henderson-Hasselbalch equation works equally well for concentrations as well as moles. In calculations involving the addition of strong acids or bases, it is better to use **moles**.

moles of HCl = 0.01000 L * 1.00 M = 0.0100 mol HCl
mol weak acid = 1.00 L * 0.700 M = 0.700 mol acetic acid
mol conjugate base = 1.00 L * 0.600 M = 0.600 mol acetate ion

Every mole of strong acid will eliminate one mol of the conjugate base, but it will also create one mole of the weak acid:

	$CH_3CO_2^{-1}$	$+ H^+$	->	CH_3CO_2H
initial moles:	0.600	0.0100		0.700
final moles:	0.590	0		0.710

You can then re-calculate the pH using the Henderson-Hasselbalch equation and the new concentrations:

$$pH = pK_a + \log\frac{[\text{Conj. base}]}{[\text{acid}]} = 4.74 + \log\frac{[0.590]}{[0.710]} = \mathbf{4.66}$$

Note that the buffer solution become more acidic upon addition of HCl; this makes intuitive sense, since HCl is a strong acid.

For the addition of strong acids, you can re-write the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{pK_a} + \log \frac{(\mathrm{mol}_{\mathrm{Conj.base}} - \mathrm{mol}_{\mathrm{strong.acid}})}{(\mathrm{mol}_{\mathrm{weak.acid}} + \mathrm{mol}_{\mathrm{strong.acid}})}$$

Example: Calculate the pH of a 1.00 L buffer with $[CH_3CO_2H]$ = 0.700 M and $[CH_3CO_2^{-1}]$ = 0.600 M, pK_a = 4.74, if 15.00 mL of 2.10 M NaOH is added?

Use moles with the Henderson-Hasselbalch equation as before.

moles of NaOH = 0.01500 L * 2.10 M = 0.0315 mol NaOH
mol weak acid = 1.00 L * 0.700 M = 0.700 mol acetic acid
mol conjugate base = 1.00 L * 0.600 M = 0.600 mol acetate ion

Every mole of strong base will eliminate one mol of the weak acid, but it will also create one mole of the conjugate base:

	CH_3CO_2H +	OH^- ->	$CH_3CO_2^-$ + H_2O
initial moles:	0.700	0.0315	0.600
final moles:	0.669	0	0.632

You can then re-calculate the pH using the Henderson-Hasselbalch equation and the new concentrations:

$$\mathrm{pH} = \mathrm{pK_a} + \log \frac{[\mathrm{Conj.\ base}]}{[\mathrm{acid}]} = 4.74 + \log \frac{[0.632]}{[0.669]} = \mathbf{4.72}$$

Note that the buffer solution become more basic upon addition of NaOH; this makes intuitive sense, since sodium hydroxide is a strong base.

For the addition of strong base, you can re-write the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{pK_a} + \log \frac{(\mathrm{mol}_{\mathrm{Conj.\ base}} + \mathrm{mol}_{\mathrm{strong\ base}})}{(\mathrm{mol}_{\mathrm{weak\ acid}} - \mathrm{mol}_{\mathrm{strong\ base}})}$$

Buffer Calculations Using Weak Bases & Conj. Acids

The Henderson-Hasselbalch equation can be re-written to accommodate buffers which incorporate a weak base and its conjugate acid. The new expression would be:

$$\mathrm{pOH} = \mathrm{pK_b} - \log \frac{[\mathrm{base}]}{[\mathrm{Conj.\ acid}]}$$

The buffer calculations are similar to those above for buffers with weak acids and conjugate bases. $pK_b = -\log K_b$, etc. Remember to switch to pH from pOH if using this version of the Henderson-Hasselbalch equation.

CH 223 Chapter Fourteen Part II Study Guide

- Be able to predict the pH of an acid-base reaction at the equivalence point:

Acid	Base	pH at equivalence point
Strong Acid	Strong Base	pH = 7 (neutral)
Strong Acid	Weak Base	pH < 7 (acidic)
Weak Acid	Strong Base	pH > 7 (basic)
Weak Acid	Weak Base	depends on the magnitudes of K_a and K_b

- Know the definition of equivalence point.
- Be able to calculate the pH at the equivalence point for the above acid - base examples.
- Be able to predict the effect on pH of adding a common ion using the idea behind the common ion effect.
- Understand how a buffer works.
- Be able to calculate the pH of a buffer solution before and after adding an acid or a base.
- Know how to use the Henderson-Hasselbalch Equation to calculate the pH of a buffer solution. Know how to utilize the equation upon changes in buffer composition.
- Know how to create a buffer of a given pH in the lab.
- Be able to calculate the pH at any point along a titration curve. This includes before adding any titrant (the initial point), during the period before equivalence point, at the equivalence point, and after the equivalence point.
- Understand the differences between titration curves for strong acids - strong bases and when using a strong - weak combination.
- Be able to describe how indicators can assist in acid-base titrations.
- Be able to solve and understand the assigned problems in problem set #3.

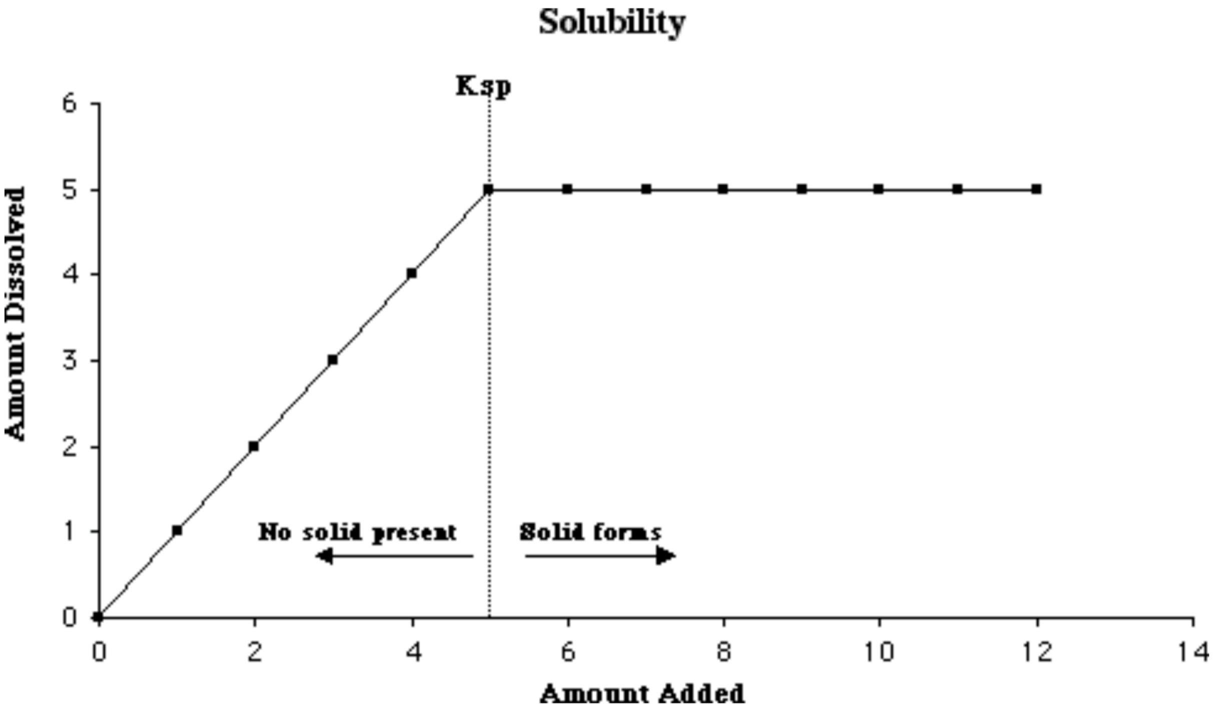
CH 223 Guide to Solubility Calculations

The extent to which an insoluble salt dissolves can be expressed in terms of the equilibrium constant. For lead(II) iodide, the expression can be written as:

$$PbI_{2(s)} \Leftrightarrow Pb^{+2}_{(aq)} + 2\ I^{-}_{(aq)} \qquad K_{sp} = [Pb^{+2}][I^{-}]^2$$

The equilibrium constant, K_{sp}, is called the **solubility product constant** or simply the **solubility constant**. The concentration of the solid, $PbI_{2(s)}$, is omitted from the equilibrium expression because it is a constant - all solids and liquids are removed from equilibrium constants.

The solubility of any compound can be observed graphically using the following diagram:



As solid is first introduced to the system, it is immediately dissolved until a certain threshold value is obtained - here referred to as "K_{sp}". Past the threshold, the solid is insoluble in the solution - no more dissolves. Each solvent has a certain capacity to dissolve solute, and the threshold value signifies the limit of the solvent to dissolve the solid solute.

Examples of typical solubility calculations follow.

1. *If 55 mg of lead(II) sulfate are placed in 250. mL of pure water, what mass of the lead compound remains undissolved?*

In a lead(II) sulfate solution, $K_{sp} = 1.8 * 10^{-8}$. The amount that dissolves, x (which is also referred to as the *solubility* of $PbSO_4$), can be expressed using K_{sp}:

$$K_{sp} = [Pb^{2+}][SO_4^{2-}] = x*x = x^2, \textit{ and}$$
$$x = (K_{sp})^{0.5} = (1.8*10^{-8})^{0.5} = 1.3*10^{-4}\text{ M}$$

This is the amount that dissolves in solution; i.e. the concentration of both lead(II) ions and sulfate ions will equal $1.3*10^{-4}$ M at equilibrium.

This concentration can be converted to grams:

$$(1.3*10^{-4}\text{ mol ions / L}) * 0.250\text{ L} * (1\text{ mol }PbSO_4 / 1\text{ mol ions}) * (303\text{ g }PbSO_4 / \text{mol }PbSO_4) =$$
$$0.010\text{ g} * (10^3\text{ mg / g}) = \mathbf{10.\ mg\ PbSO_4}$$

This answer means that 10. mg of lead(II) sulfate will dissolve in 250. mL of water. If 55 mg of lead(II) sulfate are placed in 250. mL of water, only 10. mg will dissolve. Therefore, at equilibrium

$$55\text{ mg} - 10.\text{ mg} = \mathbf{45\ mg\ undissolved\ PbSO_4}$$

Note that if only 7 mg of $PbSO_4$ were placed in 250. mL of water, all of it would dissolve. 10. mg is the **threshold** for the $PbSO_4$ system; if less than 10. mg is added, all of it dissolves, and if more than 10. mg is added, only 10. mg of it will dissolve and the remainder will exist as solid precipitate.

2. *A solution contains Ca^{2+} and Pb^{2+} ions, both at a concentration of 0.010 M. If sodium sulfate is added, which metal ion precipitates first? What is the concentration of the first ion to precipitate as the second more soluble ion begins to precipitate?*

The first step is to determine the salts that will be precipitating; these are **$CaSO_4$** ($K_{sp} = 2.4*10^{-5}$) and **$PbSO_4$** ($K_{sp} = 1.8*10^{-8}$). To find which one will precipitate first, we need to calculate the concentration of the sulfate ion necessary to initiate precipitation:

For $PbSO_4$: $[SO_4^{2-}] = K_{sp} / [Pb^{2+}] = 1.8*10^{-8} / 0.010 = \mathbf{1.8*10^{-6}\ M}$
For $CaSO_4$: $[SO_4^{2-}] = K_{sp} / [Ca^{2+}] = 2.4*10^{-5} / 0.010 = \mathbf{2.4*10^{-3}\ M}$

The concentration of sulfate required to precipitate $PbSO_4$ is *much less* than the concentration of sulfate required to precipitate $CaSO_4$; hence, **$PbSO_4$ will begin to precipitate** out of solution **before $CaSO_4$ begins to precipitate.**

To calculate the concentration of Pb^{2+} present in solution once $CaSO_4$ begins to precipitate, we need to use the concentrations of sulfate ion determined previously. $[SO_4^{2-}] = 2.4*10^{-3}$ M when $CaSO_4$ begins to precipitate, and we can use this value in the K_{sp} expression for $PbSO_4$:

$$\mathbf{[Pb^{2+}]} = K_{sp} / [SO_4^{2-}] = 1.8*10^{-8} / 2.4*10^{-3}\text{ M} = \mathbf{7.5*10^{-6}\text{ M}}$$

Notice how the concentration of lead(II) ions decreased from an initial value of 0.010 M to $7.5*10^{-6}$ M once $CaSO_4$ began to precipitate.

3. *Sodium hydroxide is added dropwise to a solution containing 0.1 M concentrations of* Fe^{3+}*,* Pb^{2+} *and* Al^{3+}*. What is the order by which the hydroxide salts begin to precipitate?*

First, find the K_{sp} values for the relevant hydroxide complexes.

$Fe(OH)_3$: $K_{sp} = 6.3*10^{-38} = [Fe^{3+}][OH^{-1}]^3$
$Pb(OH)_2$: $K_{sp} = 2.8*10^{-16} = [Pb^{2+}][OH^{-1}]^2$
$Al(OH)_3$: $K_{sp} = 1.9*10^{-33} = [Al^{3+}][OH^{-1}]^3$

Next, calculate the concentration of hydroxide necessary to initiate precipitation in each of the salts. Remember to account for the different forms of each K_{sp} expression.

For $Fe(OH)_3$: $\mathbf{[OH^{-1}]} = (K_{sp} / [Fe^{3+}])^{1/3} = (6.3*10^{-38} / 0.1)^{1/3} = \mathbf{8.6*10^{-13}\text{ M}}$
For $Pb(OH)_2$: $\mathbf{[OH^{-1}]} = (K_{sp} / [Pb^{2+}])^{1/2} = (2.8*10^{-16} / 0.1)^{1/2} = \mathbf{5.3*10^{-8}\text{ M}}$
For $Al(OH)_3$: $\mathbf{[OH^{-1}]} = (K_{sp} / [Al^{3+}])^{1/3} = (1.9*10^{-33} / 0.1)^{1/3} = \mathbf{2.7*10^{-11}\text{ M}}$

Fe^{3+} requires the *least* amount of OH^{-1} (only $8.6*10^{-13}$ M!) begin precipitation; hence, **$Fe(OH)_3$ will precipitate first**. The **second ion** to begin precipitating **will be $Al(OH)_3$, followed by $Pb(OH)_2$** which takes the most hydroxide ($5.3*10^{-8}$ M) to begin precipitating.

CH 223 Chapter Fifteen Study Guide

- Be able to write the solubility product constant expression (K_{sp}) for any insoluble salt. Recall the solubility tables from CH 221 – what do you think of them now?
- Be able to calculate K_{sp} values from experimental data.
- Know how to estimate the solubility of a salt from the value of K_{sp}.
- Be able to use the values of different K_{sp}s to predict the order of precipitation amongst various salts.
- Know how to decide if a precipitate forms when the ion concentrations are known using Q values.
- Be able to calculate the ion concentrations required to begin the precipitation of an insoluble salt.
- Be familiar with the concept of the common ion effect, and be able to calculate the solubility of a salt in the presence of a common ion.
- Know how to use K_{sp} values to devise a method of separating ions in solution from one another. This will become quite important during the last three labs of CH 223.
- Realize the differences between the solubility product constant and the formation constant (K_f). Know the definition of a complex ion and be able to recognize a complex ion in a reaction.
- Know that pH can affect the solubility of certain salts when basic anions are present. Be able to predict which salts should be soluble in strong acids, and know that most metal cations form "insoluble" hydroxide complexes (with the exception of the alkali metals and alkaline earths.)
- Recognize the reason for the quotation marks around "insoluble" in the above statement. Are the metal hydroxide salts *truly* insoluble? Do you recognize the reason for my scorn of the "solubility tables" from Chapter Five?
- Be able to solve and understand the assigned problems in problem set #4.

Understanding Entropy in CH 223

Entropy, **S**, is a measure of the disorder of a system. According to the second law of thermodynamics, the total entropy of the universe is continually increasing, so everything we do as chemists and as human beings must somehow be increasing the quantity of disorder in the universe.

The third law of thermodynamics states that the entropy of each element in some crystalline state at zero Kelvin equals zero. Realize that the chances of finding any element in this idealized (and vague!) crystalline state at 0 K is about zero, so *everything* has some measure of entropy to it; *viz.*, **the entropy of *every* substance will be greater than zero at temperatures greater than zero Kelvin.**

Some generalizations regarding entropy:

1) The entropy of gases is greater than the entropy of liquids, and the entropy of liquids is greater than the entropy of solids.
   Example: $H_20_{(g)}$: $S = 188.8\ J\ K^{-1}\ mol^{-1}$
   Example: $H_20_{(l)}$: $S = 69.9\ J\ K^{-1}\ mol^{-1}$

2) The entropy of complex molecules is greater than the entropy of simple molecules.
   Example: $C_3H_{8(g)}$: $S = 269.9\ J\ K^{-1}\ mol^{-1}$
   Example: $C_2H_{6(g)}$: $S = 229.6\ J\ K^{-1}\ mol^{-1}$
   Example: $CH_{4(g)}$: $S = 186.3\ J\ K^{-1}\ mol^{-1}$

3) In ionic solids, the weaker the ionic charges, the higher the entropy.
   Example: $MgO_{(s)}$: $S = 26.9\ J\ K^{-1}\ mol^{-1}$
   Example: $NaF_{(s)}$: $S = 51.5\ J\ K^{-1}\ mol^{-1}$
   Example: $CH_{4(g)}$: $S = 186.3\ J\ K^{-1}\ mol^{-1}$

4) Entropy usually **increases** when pure liquids or solids dissolve in a solvent.

5) When dissolved gases escape from a solution, entropy usually **increases**.

6) By the second law of thermodynamics,

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

Occasional localized decreases in entropy are acceptable as long as the overall entropy of the universe continues to increase.

The Gibbs Free Energy Equations & Relations

$\Delta G = -T\Delta S_{universe}$	Relates Gibbs Free Energy (ΔG) with the entropy of the universe ($\Delta S_{universe}$). By the second law of thermodynamics, $\Delta S_{universe}$ must always increase; therefore, ΔG must be negative for product favored reactions.
$\Delta G = \Delta H - T\Delta S$	Relates ΔG to enthalpy (ΔH) and entropy (ΔS); also known as the "two headed snake" equation. Enthalpy and entropy can combine to make some reactions always product favored ($\Delta G < 0$) or always reactant favored ($\Delta G > 0$); in addition, sometimes enthalpy and entropy "fight" one another, making the final value of ΔG temperature dependent.
$\Delta G = -RT \ln K$	Relates ΔG with the equilibrium constant (K). R = gas constant (8.3145 J K^{-1} mol^{-1}), T = temperature (K). If ΔG is product favored ($\Delta G < 0$), K is greater than 1; if ΔG is reactant favored ($\Delta G > 0$), K is less than 1.
$\Delta G = - nFE$	Relates ΔG with the potential of a chemical cell (E). n = number of electrons transferred, F = Faraday constant (96,485 C mol^{-1}). If ΔG is product favored ($\Delta G < 0$), E is greater than 0 (positive); if ΔG is reactant favored ($\Delta G > 0$), E is less than 0 (negative).
$\Delta G = \Sigma\Delta G_{products} - \Sigma\Delta G_{reactants}$	Used to calculate the Gibbs Free Energy (ΔG) for a reaction using tables of standardized ΔG values. Like enthalpy, ΔG will be zero for elements in their standard states ($O_{2(g)}$, $Mg_{(s)}$, $Br_{2(l)}$, etc. - all will have $\Delta G = 0$).

	ΔG	K	E	$\Delta S_{universe}$
Product Favored	-	> 1	+	+
Reactant Favored	+	< 1	-	-

ΔH	ΔS	ΔG
-	+	**-** (always product favored)
+	-	**+** (always reactant favored)
-	-	Depends on temperature, generally product favored at low T
+	+	Depends on temperature, generally product favored at high T

CH 223 Chapter Sixteen Study Guide

- Be able to describe the differences between kinetics and thermodynamics. What does each provide? How can they compliment each other?
- Realize that entropy is a measure of matter and/or energy dispersal. Entropy is often synonymous with disorder.
- Be able to predict the sign of the entropy change for a reaction of a change in state.
- Be able to calculate the entropy change for a change of state or for a chemical reaction.
- Recall past lectures concerning enthalpy - what is it, how it is measured, etc.
- Be able to use entropy and enthalpy changes to predict whether a reaction is product- or reactant- favored.
- Understand the subtle difference between Gibbs Free Energy and the entropy of the universe. Know how this applies to the second law of thermodynamics.
- Realize the connection between entropy, enthalpy and Gibbs Free energy. Know the definition of spontaneity and know how it applies to Gibbs free energy.
- Be able to calculate a change of entropy, enthalpy and/or Gibbs free energy from the reactants and products.
- Be able to determine the relationship between the free energy change for a reaction and its equilibrium constant.
- Be able to determine the temperature at which a reaction can become product favored, if applicable.
- Be able to solve and understand the assigned problems in problem set #4 & #5.

("q&d") Redox Reactions Guide for CH 223

"q&d" = "Quick 'n' Dirty"

Part I: General Instructions - *for reactions where pH is not important*

1) Recognize that the reaction is an oxidation-reduction reaction. Look for changes in oxidation number on similar atoms in both the reactant and product side.

Example: $HCl + NaOH \rightarrow H_2O_{(l)} + NaCl$ *not an oxidation-reduction reaction*
Example: $Ag^+ + Cu_{(s)} \rightarrow Ag_{(s)} + Cu^{2+}$ *oxidation-reduction*

2) Separate the process into two **half-reactions**. One side will be a **reduction** and the other will be an **oxidation**.

Example: $Ag^+ \rightarrow Ag_{(s)}$
$Cu_{(s)} \rightarrow Cu^{2+}$

3) Balance each half-reaction for **mass** (atoms) and **charge** (using electrons).

Example: $Ag^+ + e^- \rightarrow Ag_{(s)}$ *reduction*
$Cu_{(s)} \rightarrow Cu^{2+} + 2\,e^-$ *oxidation*

4) Multiply each half-reaction by a factor that makes the number of electrons equal.

Example: $Ag^+ + e^- \rightarrow Ag_{(s)}$
$Cu_{(s)} \rightarrow Cu^{2+} + 2\,e^-$
If we multiply the first reaction by **2** and the second reaction by **1**, the number of electrons in each half-reaction will be equal.
$2\,Ag^+ + 2\,e^- \rightarrow 2\,Ag_{(s)}$
$Cu_{(s)} \rightarrow Cu^{2+} + 2\,e^-$

5) Add the two half-reactions to create the overall balanced equation. The equation should be balanced for mass and devoid of electrons.

Example: $2\,Ag^+ + \cancel{2\,e}^- \rightarrow 2\,Ag_{(s)}$
$Cu_{(s)} \rightarrow Cu^{2+} + \cancel{2\,e}^-$

$\mathbf{2\,Ag^+ + Cu_{(s)} \rightarrow 2\,Ag_{(s)} + Cu^{2+}}$

6) Confirm that mass and charge are balanced in the overall equation.

Example: 2 silver atoms on reactant and product side
1 copper atom on reactant and product side
mass balanced
2(+1) = +2 charge on reactant side
+2 charge on product side
charge balanced

<u>Part II</u>: Acidic Conditions - *for reactions where pH < 7*

1) Recognize that the reaction is an oxidation-reduction reaction. Look for changes in oxidation number on similar atoms in both the reactant and product side.

Example: $VO_2^+ + Zn_{(s)} \rightarrow VO^{2+} + Zn^{2+}$ *oxidation-reduction*

2) Separate the process into two **half-reactions**. One side will be a **reduction** and the other will be an **oxidation**.

Example: $VO_2^+ \rightarrow VO^{2+}$
$Zn_{(s)} \rightarrow Zn^{2+}$

3) Balance each half-reaction for **mass** (atoms) and **charge** (using electrons). Note that in *acidic solution*, mass can be balanced by using water and H^+ if appropriate. Water will go to the side that is *oxygen deficient*, and hydrogen ions will go to the side that is *hydrogen deficient*. Some half-reactions will not need any water or hydrogen ions.

Example: $2\,H^+ + VO_2^+ + e^- \rightarrow VO^{2+} + H_2O_{(l)}$ *reduction*
$Zn_{(s)} \rightarrow Zn^{2+} + 2\,e^-$ *oxidation*

4) Multiply each half-reaction by a factor that makes the number of electrons equal.

Example: $2\,H^+ + VO_2^+ + e^- \rightarrow VO^{2+} + H_2O_{(l)}$
$Zn_{(s)} \rightarrow Zn^{2+} + 2\,e^-$
If we multiply the first reaction by **2** and the second reaction by **1**, the number of electrons in each half-reaction will be equal.
$4\,H^+ + 2\,VO_2^+ + 2\,e^- \rightarrow 2\,VO^{2+} + 2\,H_2O_{(l)}$
$Zn_{(s)} \rightarrow Zn^{2+} + 2\,e^-$

5) Add the two half-reactions to create the overall balanced equation. The equation should be balanced for mass & devoid of electrons. Cancel water and/or protons if present on both sides of the equation.

Example: $4\,H^+ + 2\,VO_2^+ + \cancel{2\,e^-} \rightarrow 2\,VO^{2+} + 2\,H_2O_{(l)}$
$Zn_{(s)} \rightarrow Zn^{2+} + \cancel{2\,e^-}$

$4\,H^+ + 2\,VO_2^+ + Zn_{(s)} \rightarrow 2\,VO^{2+} + 2\,H_2O_{(l)} + Zn^{2+}$

6) Confirm that mass and charge are balanced in the overall equation.

Example: 4 hydrogen atoms on each side
2 vanadium atoms on each side
4 oxygen atoms on each side
1 zinc atom on each side
mass balanced
4(+1) + 2(+1) = +6 charge on reactant side
2(+2) +2 = +6 charge on product side
charge balanced

<u>Part III</u>: Basic Conditions - *for reactions where pH > 7*

1) Recognize that the reaction is an oxidation-reduction reaction. Look for changes in oxidation number on similar atoms in both the reactant and product side.

Example: MnO_4^- + HO_2^- -> MnO_4^{2-} + O_2 *oxidation-reduction*

2) Separate the process into two **half-reactions**. One will be a **reduction** and the other an **oxidation**.

Example: MnO_4^- -> MnO_4^{2-}
HO_2^- -> O_2

3) Balance each half-reaction for **mass** (atoms) and **charge** (using electrons). Note that in *basic solution*, mass can be balanced by using water and OH^- if appropriate. Hydroxide will go to the side that is *oxygen deficient*, and water will go to the side that is *hydrogen deficient*. Some half-reactions will not need any water or hydrogen ions.

Example: MnO_4^- + e^- -> MnO_4^{2-} *reduction*
OH^- + HO_2^- -> O_2 + 2 e^- + $H_2O_{(l)}$ *oxidation*

4) Multiply each half-reaction by a factor that makes the number of electrons equal.

Example: MnO_4^- + e^- -> MnO_4^{2-}
OH^- + HO_2^- -> O_2 + 2 e^- + $H_2O_{(l)}$
If we multiply the first reaction by **2** and the second reaction by **1**, the number of electrons in each half-reaction will be equal.
2 MnO_4^- + 2 e^- -> 2 MnO_4^{2-}
OH^- + HO_2^- -> O_2 + 2 e^- + $H_2O_{(l)}$

5) Add the two half-reactions to create the overall balanced equation. The equation should be balanced for mass and devoid of electrons. Cancel water and/or hydroxide if present on both sides of the equation.

Example: 2 MnO_4^- + $\cancel{2e}^-$ -> 2 MnO_4^{2-}
OH^- + HO_2^- -> O_2 + $\cancel{2e}^-$ + $H_2O_{(l)}$
----
2 MnO_4^- + OH^- + HO_2^- -> 2 MnO_4^{2-} + O_2 + $H_2O_{(l)}$

6) Confirm that mass and charge are balanced in the overall equation.

Example: 2 manganese atoms on each side
11 oxygen atoms on each side
2 hydrogen atoms on each side - *mass balanced*
2(-1) + (-1) + (-1) = -4 charge on reactant side
2(-2) = -4 charge on product side - *charge balanced*

7) *Alternatively*, you may balance basic redox reactions using the acidic process used in Part II. Upon completing step 5, add OH^{--} to neutralize any H^+ present. Add a similar amount of OH^- to both sides. All of the H^+ will be converted to H_2O, and the opposite side should have OH^- present.

The Nernst Equation

Not all systems are at equilibrium when measured. Slow kinetics, adding or removing of substrate, and other factors can keep the system from attaining equilibrium - for a while.

Values of E^o are applicable *only* to equilibrium conditions. To calculate cell potentials for non-equilibrium systems, we use the **Nernst Equation**:

$$\mathbf{E = E^o - (RT/nF) \ln Q}$$

where
E = cell potential (V) at nonstandard conditions
E^o = cell potential (V) at standard equilibrium conditions
R = Gas constant (8.314 J/K mol)
T = Temperature (K)
F = Faraday constant (96,485 C/mol e^-)
n = the number of moles of electrons transferred
Q = reaction quotient; for the reaction: $a\,A_{(aq)} + b\,B_{(aq)} <=> c\,C_{(aq)} + d\,D_{(aq)}$,

$$\text{then } \mathbf{Q} = \frac{[\mathbf{C}]^{\mathbf{c}}[\mathbf{D}]^{\mathbf{d}}}{[\mathbf{A}]^{\mathbf{a}}[\mathbf{B}]^{\mathbf{b}}}$$

Example: Find **E** when $[Zn^{2+}] = 0.0010$ M, $P(H_2) = 0.10$ atm and pH = 0 at 298 K.

$\mathbf{[H^+]} = 10^{-pH}$ M = 10^{-0} M = **1.0 M**; note that **n = 2**

$Zn_{(s)} \text{ ---> } Zn^{2+}_{(aq)} + 2e^-$ $E^0 = 0.76$ V
$2\,H^+_{(aq)} + 2e^- \text{ ---> } H_{2(g)}$ $E^0 = 0.00$ V

$\mathbf{2\,H^+_{(aq)} + Zn_{(s)} \text{ ---> } Zn^{2+}_{(aq)} + H_{2(g)}}$ $E_{net}^{\ 0} = 0.76$ V

Use the Nernst equation to find E:

$$E = E^o - (RT/nF) \ln Q$$

$$Q = \frac{\left[Zn^{2+}\right]P_{H_2}}{\left[H^+\right]^2} = [0.0010 * 0.10 / (1.0)^2] = 0.00010$$

$$E = 0.76 \text{ V} - (8.314 * 298 \text{ K} / 2 * 96500) \ln 0.00010$$
$$E = 0.76 \text{ V} + 0.12 \text{ V} = \mathbf{0.88\ V}$$

CH 223 Chapter Seventeen Study Guide

- Be able to define and use the terms battery, electrochemical cell, fuel cell, electrolysis, electrode, electrolyte, salt bridge, anode and cathode.

- **MEMORIZE** the value of the Faraday Constant, F = 96,485 C mol^{-1} electrons.

- Be able to balance oxidation-reduction reactions in acidic or basic solutions using the half-reaction approach.

- Realize the internal workings of an electrochemical cell.

- Be able to appreciate the meaning of standard electrode potential and its connection to the free energy change for a cell reaction. Know the meaning of the SHE in electrochemistry.

- Realize that product favored reactions have a positive E value while reactant favored reactions have a negative E value.

- Know that when a half-reaction or net electrochemical reaction is reversed, the sign of E is reversed but its value does not change.

- Know how to compare two chemical species for the relative strength of oxidizing agents.

- Recognize that electrochemical potentials depend on the nature of the reactants and products and their concentrations, not their quantities of material used.

- Be able to use the Nernst equation to calculate the cell potential under nonstandard conditions.

- Be able to calculate the equilibrium constant for a reaction from the value of E.

- Be able to describe the difference between electrolysis of an electrolyte and the operation of a galvanic or voltaic cell.

- Know how to use the relationship between current, electric charge, and time and occasionally the Faraday constant.

- Be able to solve and understand the assigned problems in problem set #5.

CH 223 Chapter Eighteen Study Guide

- Identify the main group metals, metalloids and non-metals. Be able to predict properties for each of these classifications.

- Know the general periodic properties for each of the classifications listed above.

- Realize which reactions produce ionic compounds and which will probably produce covalent compounds.

- Be able to predict formulas for common ions using their electron configuration and oxidation number.

- Know where to find information regarding a series of main group elements, including bonding character (ionic or covalent), color, solubility ("like attracts like"), simple reaction chemistry, etc.

- Realize the importance of chemicals in the daily lives of human beings. Understand how the chemistry relates to the usage of the product.

- Be able to solve and understand the assigned problems in problem set #6.

Coordination Compounds Nomenclature Guide

1) In naming a coordination compound that is a salt, name the cation first and the anion second.

2) When giving the name of the complex ion or molecule, name the ligands first, in alphabetical order, followed by the name of the metal.

   a. If a ligand is an anion whose name ends in *-ite* or *-ate*, the final *e* is changed to *o*
      Example: "sulfate" becomes "sulfato", "nitrate" becomes "nitrato", etc.
   b. If a ligand is an anion whose name ends in *-ide*, the *-ide* is changed to *o*
      Example: "chloride" becomes "chloro", "cyanide" becomes "cyano", etc.
   c. If a ligand is a neutral molecule, its common name is usually used.
      Exceptions: water becomes *aqua*
      ammonia becomes *ammine*
      carbon monoxide becomes *carbonyl*
   d. When more than one simple monodentate ligand, use di, tri, tetra, etc. prefix.
   e. When more than one complex ligand, use bis, tris, tetrakis, pentakis, etc. prefix.

3) If the complex ion is an anion, the suffix *-ate* is added to the metal name.

4) Following the name of the metal, the oxidation number of the metal is given in Roman numerals.

Examples of Coordination Compounds:

$[Ni(H_2O)_6]SO_4$	Hexaaquanickel(II) sulfate
$K_2[CoCl_4]$	Potassium tetrachlorocobaltate(II)
$Ba[BrF_4]_2$	Barium tetraflurobromate(III)
$Li[CrF_4O]$	Lithium tetrafluorooxochromate(V)
$[Ru(NH_3)_5N_2]Cl_2$	Pentaamminedinitrogenruthenium(II) chloride
$K[Pt(NH_3)Cl_3]$	Potassium amminetrichloroplatinate(II)
$Co(phen)_2Cl_2$	Dichlorobis(phenanthroline)cobalt(II)

CH 223 Chapter Nineteen Study Guide

- Identify the transition elements, the *d*-block elements, the lanthanide elements, the actinide elements, and the *f*-block elements. Be able to predict properties for each of these classifications.

- Know how to determine if an element is paramagnetic or diamagnetic.

- Be able to describe and identify coordination compounds. Know how to determine the oxidation number for a coordination compound.

- Know what a ligand is and whether it is monodentate, bidentate or polydentate.

- Understand why there are no cationic coordination compounds.

- Know what EDTA is.

- Know how to systematically name coordination complexes using the rules outlined in the handout.

- Be able to determine the coordination number for a coordination compound. Know the differences between octahedral, square planar and tetrahedral complexes.

- Understand the definition of an isomer. Realize that there are two types of isomers, both geometrical and optical.

- Know the terms *cis*, *trans*, *mer*, and *fac*. Know how they apply to isomerism in coordination compounds.

- Be able to explain briefly the differences between molecular orbital theory and crystal field theory.

- Know what differentiates between high spin and low spin complexes.

- Understand why coordination compounds are colored and how the complex can be explained using the crystal field model of bonding.

- Be able to solve and understand the assigned problems in problem set #6.

- Realize that this is the last chapter study guide that you will ever see in a Chem 22x class! On to the final exam and summer break!!!

CH 223 Chapter Thirteen Concept Guide

1. Writing Equilibrium Constant Expressions

Problem

Write the equilibrium constant (K_c) expressions for each of the following reactions:

(a) $Cu(OH)_2(s) \rightleftarrows Cu^{2+}(aq) + 2\ OH^-(aq)$

(b) $Cu(NH_3)_4{}^{2+}(aq) \rightleftarrows Cu^{2+}(aq) + 4\ NH_3(aq)$

(c) $CH_3CO_2H(aq) + H_2O(\ell) \rightleftarrows CH_3CO_2{}^-(aq) + H_3O^+(aq)$

Solution

(a) $K_c = [Cu^{2+}]\,[OH^-]^2$

(b) $$K_c = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4{}^{2+}]}$$

(c) $$K_c = \frac{[CH_3CO_2{}^-][H_3O^+]}{[CH_3CO_2H]}$$

2. Writing Equilibrium Constant Expressions

Problem

Write the equilibrium constant (K_c) expressions for each of the following reactions:

(a) $$CO(g) + \frac{1}{2}O_2(g) \rightleftarrows CO_2(g)$$

(b) $C(s) + CO_2(g) \rightleftarrows 2\ CO(g)$

(c) $FeO(s) + CO(g) \rightleftarrows Fe(s) + CO_2(g)$

Solution

(a) $$K_c = \frac{[CO_2]}{[CO][O_2]^{1/2}}$$

(b) $$K_c = \frac{[CO]^2}{[CO_2]}$$

(c) $$K_c = \frac{[CO_2]}{[CO]}$$

3. Writing Equilibrium Constant Expressions

Problem

Write the equilibrium constant (K_c) expressions for each of the following reactions:

(a) $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$

(b) $2\ NO(g) + Br_2(g) \rightleftharpoons 2\ NOBr(g)$

(c) $2\ HF(g) \rightleftharpoons H_2(g) + F_2(g)$

Solution

(a) $$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

(b) $$K_c = \frac{[NOBr]^2}{[NO]^2[Br_2]}$$

(c) $$K_c = \frac{[H_2][F_2]}{[HF]^2}$$

4. Interpreting the Value of K

Question

A student's task was to remove silver ion for an aqueous solution as completely as possible by causing it to form a precipitate. Given the following information, which would be the better method: to add a solution containing sulfate ion or one containing an equivalent amount of sulfide ion?

$Ag_2SO_4(s) \rightleftharpoons 2\ Ag^+ + SO_4^{2-}$ $K = 1.5 \times 10^{-5}$

$Ag_2S(s) \rightleftharpoons 2\ Ag^+ + S^{2-}$ $K = 7.1 \times 10^{-50}$

Solution

The precipitates formed would be silver sulfate and silver sulfide upon addition of sulfate ion or sulfide ion, respectively. Comparison of the equilibria that would result after precipitate formation using the two K values shows that the sulfide would leave a far lower concentration of Ag^+ in solution after the precipitation reaction went to completion. Thus, the student should choose the silver and sulfide reaction:

$Ag_2S(s) \rightleftharpoons 2\ Ag^+ + S^{2-}$

5. Manipulation of Equilibrium Expressions

Question

Consider the following equilibria involving $SO_2(g)$ and their corresponding equilibrium constants.

(1) $SO_2(g) + {}^{1}/_{2}\, O_2(g) \rightleftarrows SO_3(g) \quad K_1$

(2) $2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g) \quad K_2$

Which of the following expressions relates K_1 to K_2?

(a) $K_2 = K_1^2$

(b) $K_2^2 = K_1$

(c) $K_2 = \frac{1}{K_1}$

(d) $K_2 = \frac{1}{K_1^2}$

Solution

Reaction 2 is the inverse of reaction 1, and squared. Thus, (d) is the correct answer. K_2 is related to K_1 by:

$$K_2 = \frac{1}{K_1^2}$$

6. Writing Equilibrium Constant Expressions

Problem

Calculate K for the reaction

$SnO_2(s) + 2\ CO(g) \rightleftarrows Sn(s) + 2\ CO_2(g)$

given that:

$SnO_2(s) + 2\ H_2(g) \rightleftarrows Sn(s) + 2\ H_2O(g) \quad K = 8.12$

$H_2(g) + CO_2(g) \rightleftarrows CO(g) + H_2O(g) \quad K = 0.771$

Solution

In general, when two or more equations are added to produce a net equation, the equilibrium constant for the net equation is the product of the equilibrium constants for the added equations. In this case, we need to reverse and double the second reaction to add to the first reaction.

$$\begin{array}{ll} SnO_2(s) + 2\,H_2(g) \rightleftharpoons Sn(s) + 2\,H_2O(g) & K = 8.12 \\ 2\,CO(g) + 2\,H_2O(g) \rightleftharpoons 2\,H_2(g) + 2\,CO_2(g) & K = \dfrac{1}{(0.771)^2} \\ \hline SnO_2(s) + 2\,CO(g) \rightleftharpoons Sn(s) + 2\,CO_2(g) & K = (8.12)\left(\dfrac{1}{(0.771)^2}\right) \end{array}$$

For this reaction, K=13.7

7. Evaluation of the Value of K

Question

The equilibrium constant for the formation of gaseous lithium iodide by combination of the elements in the gas phase at 3000 K is given as:

$Li(g) + {}^{1}/_{2}\,I_2(g) \rightleftharpoons LiI(g) \quad K_p = 644$

(a) What is the equilibrium constant value for this reaction if it is represented by the equation given above multiplied by a factor of 2?

(b) What is the equilibrium constant value for the reverse of the reaction as written above?

Solution

(a) Multiplying the reaction by a factor of 2 requires that the given value of K_p be squared:

$K_p = (644)^2 = 4.15 \times 10^5$

$2\,Li(g) + {}^{1}/_{2}\,I_2(g) \rightleftharpoons 2\,LiI(g) \quad K_p = (644)^2$

(b) When the equation is reversed, K_p becomes the reciprocal of the original value:

$$K_p = \frac{1}{644} = 1.55 \times 10^{-3}$$

$LiI(g) \rightleftharpoons Li(g) + {}^{1}/_{2}\,I_2(g) \qquad K_p = \dfrac{1}{644}$

8. Reaction Quotient

Problem

The concentration equilibrium constant (K_c) for the reaction

$ClF_3(g) \rightleftharpoons ClF(g) + F_2(g)$

is 8.77×10^{-14} at 25 °C. Describe what happens quantitatively when a solution is prepared so that it is 17.50 M in ClF_3,1.3×10^{-6} M in ClF,and 4.72×10^{-7} M in F_2.

Approach
Calculate the reaction quotient, Q, and compare it to K.

Solution
The reaction quotient for the solution is:

$$Q = \frac{[ClF][F_2]}{[ClF_3]} = (1.3 \times 10^{-6}\ M)\frac{(4.72 \times 10^{-7}\ M)}{(17.50\ M)} = 3.5 \times 10^{-14}$$

$Q < K_c$, therefore the concentrations of the reactants will decrease and those of the products will increase, and the reaction will proceed toward equilibrium in the forward direction. In this case, ClF_3 will decompose until equilibrium is reached.

9. Equilibrium Concentrations

Question
Chlorine gas, Cl_2, dissociates into chlorine atoms in a reversible reaction for which K = 0.37 at 3000 K. What is the concentration of chlorine atoms in a vessel that originally contained 1.0 M of molecular chlorine?

Approach
First, write the balanced equation. Then write the corresponding equilibrium expression and identify what is unknown. Make a table to include the chemical equation, initial concentrations, changes in concentration, and equilibrium concentrations. Substitute the equilibrium concentrations from the table into the equilibrium expression and solve for the unknown (x). If an approximation was made, remember to check for validity. Finally, answer the question in the problem using some form of the value of x.

Solution
The reaction is $Cl_2(g) \rightleftharpoons 2\ Cl(g)$. The unknown is [Cl] at equilibrium, and we choose the concentration of Cl_2 that dissociates into Cl as x. The algebraic expression that must be solved for is found by arranging the known and the unknown as shown in this lesson.

	Cl_2	**$\rightleftharpoons$**	**2 Cl(g)**
Initial	1.0 M		0 M
Change	- x		+ 2x
Equilibrium	1.0 - x		2x

The equilibrium constant is represented as:

$$K = \frac{[Cl]^2}{[Cl_2]} = \frac{(2x)^2}{(1.0 - x)} = 0.37$$

Inspection shows that the values of K and the known concentration are similar in magnitude, therefore this problem should be solved using the quadratic equation.

$4x^2 = (0.37)(1.0 - x)$

$4x^2 + 0.37x - 0.37 = 0$

With a = 4, b = 0.37, and c = -0.37, the quadratic equation is:

$$\frac{-0.37 \pm \sqrt{(0.37)^2 - (4)(4)(-0.37)}}{(2)(4)}$$

$$\frac{-0.37 \pm 2.5}{8}$$

x = 0.27 M or -0.36 M

Therefore, $[Cl]_2 = 2x = (2)(0.27\ M) = 0.54\ M$.

Finally, check this answer by substituting all concentrations into the equilibrium expressions and compare.

$$K = \frac{[Cl]^2}{[Cl_2]} = \frac{(0.54)^2}{(1.0 - 0.27)} = 0.40$$

10. Le Chatelier's Principle: Factors That Influence Equilibria - Concentration

Problem

A reaction of potassium chromate and hydrochloric acid was allowed to come to equilibrium:

$$\underset{\substack{\text{chromate ion}\\ \text{yellow}}}{2\,CrO_4^{2-}} + H^+ \rightleftharpoons \underset{\substack{\text{dichromate ion}\\ \text{orange}}}{Cr_2O_7^{2-}} + H_2O(\ell)$$

Describe the changes that will occur in the equilibrium system when:

(a) additional acid is added

(b) additional potassium chromate is added

(c) zinc is added (note that $ZnCrO_4$ is highly insoluble and $ZnCr_2O_7$ is very soluble)

(d) NaOH is added

Solution

(a) Some of the additional H^+ will react with the remaining chromate ion to produce more dichromate ion and water. $[CrO_4^{2-}]$ will decrease and $[Cr_2O_7^{2-}]$ will increase.

(b) Some of the additional chromate ion will react with some of the H^+ to produce more dichromate ion. Water and $[H^+]$ will decrease.

(c) Addition of Zn^{2+} will remove some of the chromate ion as $ZnCrO_4$. This will lower the concentration of chromate ion. Thus, some of the dichromate ion will react to form additional chromate ion and H^+.

(d) Addition of NaOH will remove some of the H^+ as a result of an acid-base reaction. The decrease in $[H^+]$ will yield a reaction of additional $Cr_2O_7^{2-}$ with H_2O. $[Cr_2O_7^{2-}]$ will decrease and $[CrO_4^{2-}]$ will increase.

11. Le Chatelier's Principle: Factors That Influence Equilibria -Temperature and Pressure

Question

For the reaction

$2\ \mathrm{Hg}(\ell) + \mathrm{O_2}(g) \rightleftharpoons 2\ \mathrm{HgO}(s)$

$\Delta H°$ = - 180.7 kJ over a temperature range of 298 K to 500 K. $K_p = 3.2 \times 10^{20}$ at 298 K.

(a) Is the value of K_p at 500 K expected to be greater or less than the value of K_p at 298 K?

(b) Will a decrease in the partial pressure of O_2 cause the reaction to shift to the left or to the right?

Solution

(a) This is an exothermic reaction, thus heat can be considered a "product."

$2\ \mathrm{Hg}(\ell) + \mathrm{O_2}(g) \rightleftharpoons 2\ \mathrm{HgO}(s) + 180.7\ \mathrm{kJ}$

Increasing the temperature favors the endothermic reaction, or the reverse reaction in this case. Therefore, the equilibrium will be shifted toward the reactant side (left) as the temperature is increased. The value of K_p is expected to be less than 3.2×10^{20}. (The value of K_p at 500 K is 5.1×10^{-7}.)

(b) Decreasing the pressure favors an increase in the amount of gas present. In this case, the reverse reaction (shift to the left) would be favored.

12. Le Chatelier's Principle: Factors That Influence Equilibria - Concentration, Temperature, and Volume

Problem The value of K_p for the following reaction is 0.16 at 25 °C. The enthalpy change for the reaction at standard conditions is +16.1 kJ.

$2\ \mathrm{NOBr}(g) \rightleftharpoons 2\ \mathrm{NO}(g) + \mathrm{Br_2}(g)$

To which direction will the equilibrium shift (left, right, or no change) and how will K change when each of the following changes to the system is made?

(a) Adding more $Br_2(g)$

(b) Removing some NOBr(g)

(c) Decreasing the temperature

(d) Increasing the container volume

Approach

This is an endothermic reaction, thus heat is considered a "reactant."

$+ 16.1\ \mathrm{kJ} + 2\ \mathrm{NOBr}(g) \rightleftharpoons 2\ \mathrm{NO}(g) + \mathrm{Br_2}(g)$

Solution

(a) Left. Some of the added "product" will be consumed, thus the equilibrium will shift to the left. There will be no change in K.

(b) Left. Here, a "reactant" is being depleted. The equilibrium will shift to the left. K will not change.

(c) Left. When the temperature decreases, the system responds by shifting in the direction that leads to generation of thermal energy. The equilibrium shifts left and the value of K decreases.

(d) Right. Increasing the volume of the flask will result in a shift to the side of the equilibrium with more gas molecules. There are three moles of gas on the right and only two on the left. K will not change.

CH 223 Chapter Fourteen Part I Concept Guide

1. Identifying Brønsted-Lowry Acids and Bases

Problem

Identify the Brønsted-Lowry acid (a reactant) and its conjugate base (a product) in each of the following reactions:

(a) $HNO_3(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+ + NO_3^-$
(b) $H_3O^+ + HS^- \rightleftharpoons H_2S(aq) + H_2O(\ell)$
(c) $HF(aq) + OH^- \rightleftharpoons H_2O(\ell) + F^-$

Solution

The Brønsted-Lowry acids are the species that donates the proton in each reaction. In the above reactions, the Brønsted-Lowry acids are:

(a) HNO_3
(b) H_3O^+
(c) HF

The conjugate base for each acid is the species formed by the removal of a proton from the acid:

(a) NO_3^-
(b) H_2O
(c) F^-

2. Ion Product Constant of Water

Question

What is the concentration of OH^- in a 0.04 M HCl solution?

Approach

Because HCl is a strong acid and is 100% ionized, the H_3O^+ concentration is equivalent to the molarity of the HCl solution, 0.04 M. To solve this problem, use the relationship between the concentrations of H_3O^+ and OH^- and water: $K_w = [H_3O^+]\,[OH^-]$.

Solution

$K_w = [H_3O^+]\,[OH^-]$

Solving this for OH^- and substituting the known values of K_w and $[H_3O^+]$ gives

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{0.04} = 3 \times 10^{-13}\ M$$

3. pH and pOH

Question

What are the pH and $[H_3O^+]$ of a solution that has $[OH^-] = 2.50 \times 10^{-5}$ M?

Solution

pOH = -log $[OH^-]$ = - log (2.50×10^{-5} M) = 4.60

pH = 14.00 - pOH = 14.00 - 4.60 = 9.40

log $[H_3O^+]$ = - pH = -9.40

$[H_3O^+] = 3.98 \times 10^{-10}$

4. K_a-K_b Relationship

Problem

The value of K_a for hydrocyanic acid (HCN) is 6.2×10^{-10}. Calculate the value of K_b for the conjugate base.

Solution

$HCN(aq) + H_2O(\ell) \rightleftharpoons H_3O^+ + CN^-$

In this reaction, the conjugate base is the cyanide ion, CN^-. The value of K_b for the reaction of CN^- as a base with water is:

$CN^- + H_2O(\ell) \longrightarrow HCN(aq) + OH^-$

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

The value of K_b for the conjugate base, CN^-, is 1.6×10^{-5}.

5. Calculating pH

Question

If the hydronium ion concentration in vinegar is 1.8×10^{-3}, what is its pH?

Solution

pH = - log $[H_3O^+]$ = - log (1.8×10^{-3}) = 2.74

6. Calculating pH

Problem

Find the pH of a 0.052 M hypobromous acid (HBrO) solution.

$HBrO(aq) + H_2O(\ell) \rightleftharpoons H_3O^+ + BrO^-$ $K_a = 2.2 \text{ x } 10^{-9}$

Approach

Write the corresponding equilibrium expression and identify what is unknown. Make a table to include the chemical equation, initial concentrations, changes in concentration, and equilibrium concentrations. Substitute the equilibrium concentrations from the table into the equilibrium expression and solve for the unknown (x). If an approximation was made, remember to check for validity. Finally, answer the question in the problem using some form of the value of x.

Solution

The unknown is $[H_3O^+]$ at equilibrium. Letting $x = [H_3O^+]$,

	$HBrO(aq) \rightleftharpoons$	**H_3O^+**	**$+ BrO^-$**
Initial	0.052 M	0 M	0 M
Change	- x	+ x	+ x
Equilibrium	0.052 - x	x	x

$$K_a = \frac{[H_3O^+][BrO^-]}{[HBrO]} = \frac{(x)(x)}{(0.052 - x)} = 2.2 \times 10^{-9}$$

$$\text{If } \frac{K_a[\text{initial}]}{1000}, \text{ then } K_a = \frac{x^2}{[\text{initial}] - x} \cong \frac{x^2}{[\text{initial}]}$$

Assuming that (0.052 - x) is approximately equal to 0.052,

$x^2 = (0.052)(2.2 \text{ x } 10^{-9}) = 1.1 \text{ x } 10^{-10}$ M

$x = 1.1 \text{ x } 10^{-5}$ M

$pH = - \log [H_3O^+] = \log (1.1 \text{ x } 10^{-5}) = 4.95$

The pH of this solution is 4.95.

7. Predicting the pH of Salt Solutions

Problem

Predict whether each salt listed below has a pH greater then, less than, or equal to 7.

(a) $FeCl_3$

(b) NH_4NO_3

(c) Na_2HPO_4

Solution

(a) Fe^{3+} ion is acidic and Cl^- ion is neutral. Therefore $FeCl_3$ is acidic, and the pH is less than 7.

(b) NH_4^+ is acidic and NO_3^- is neutral. Therefore, NH_4NO_3 is acidic, and the pH is less than 7.

(c) Na^+ is neutral and HPO_4^{2-} is basic. Therefore, Na_2HPO_4 is basic, and the pH is greater than 7.

8. Identifying Lewis Bases

Problem

Each of the following is a Lewis acid-base reaction:

(a) $Ni^{2+}(aq) + 4\ CN^-(aq) \rightarrow Ni(CN)_4^{2-}(aq)$

(b) $NH_3(aq) + H^+ \rightarrow NH_4^+$

(c) $BF_3(aq) + F^- \rightarrow BF_4^-$

(d) $H^+ + OH^- \rightarrow H_2O(\ell)$

Solution

(a) CN^- is the base. An electron pair is donated by the carbon atom to the nickel ion.

(b) In Lewis acid-base terms, the free hydrogen ion is thought of as the electron-pair acceptor. Here, NH_3 is the base and the electron-pair donor.

(c) The fluoride ion donates a pair of electrons to the boron atom and is therefore the base.

(d) The H^+ ion is an electron-pair acceptor, a Lewis acid. The OH^- ion is an electron-pair donor, a Lewis base. This shows that water-ion acids and bases are also Lewis acids and bases.

9. Lewis Acids and Bases

Problem

Determine whether each substance below should be classified as a Lewis acid or base.

(a) Mn^{2+}

(b) CH_3NH_2

(c) H_2NOH in the reaction: $H_2NOH(aq) + HCl(aq) \rightarrow [H_3NOH]Cl(aq)$

(d) SO_2 in the reaction: $SO_2(g) + BF_3(g) \rightarrow O_2S\text{-}BF_3(s)$

Solution

(a) Lewis acid. Mn^{2+} is expected to accept an electron pair because it is positively charged.

(b) Lewis base. CH_3NH_2 is anticipated to donate an electron pair. The N atom has a long electron pair with which it can form a bond with a Lewis acid.

(c) Lewis base. In the reaction, H_2NOH donates an electron pair to the H^+ ion of HCl to form the adduct, $[H_3NOH]Cl$.

(d) Lewis base. SO_2 has a lone electron pair on the central S atom. In the reaction, SO_2 donates an electron pair to form the adduct, $O_2S\text{-}BF_3$.

10. Classifying Lewis Acid-Base Reactions

Question

Which of the following reactions are Lewis acid-base reactions? Identify the Lewis base in each of the acid-base reactions.

(a) $Ag^+ + 2\ NH_3 \rightarrow [Ag(NH_3)_2]^+$

(b) $I^- + I_2 \rightarrow I_3^-$

(c) $H_3O^+ + OH^- \rightarrow 2\ H_2O$

(d) $H^+ + H_2O \rightarrow H_2 + OH^-$

Answer

All the above reactions are Lewis acid-base reactions. The Lewis bases, the species that donate an electron pair to form a bond with another species, are:

(a) NH_3

(b) I^-

(c) OH^-

(d) H_2O

CH 223 Chapter Fourteen Part II Concept Guide

1. Common Ion Effect

Question

What is the pH of a solution that is 0.10 mol/L in NH_3 and 0.10 mol/L in NH_4NO_3?
$K_b = 1.8 \text{ x } 10^{-5}$ for NH_3 at 23 °C.

$NH_3(aq) + H_2O(\ell)) \rightleftarrows NH_4^+ + OH^-$

Solution

The ammonia-water equilibrium controls the pH.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Let x = OH^-. The ammonium ion concentration at equilibrium is the addition of the amount formed by the above reaction to the amount added as ammonium nitrate. The ammonium nitrate is soluble and a strong electrolyte, thus adding to the total ammonium ion concentration.

	$NH_3(aq) + H_2O(\ell) \rightleftarrows$	NH_4^+ +	OH^-
Initial	0.10	0.10	0
Change	- x	+ x	+ x
Equilibrium	0.10 - x	0.10 + x	x

Substituting these values into the equilibrium constant expression:

$$K_b = \frac{(0.10 + x)(x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

Assuming that x is small relative to the initial NH_3 and NH_4^+ concentrations, this equation becomes

$$K_b = \frac{(0.10)(x)}{(0.10)} = 1.8 \times 10^{-5}$$

$OH^- = x = 1.8 \text{ x } 10^{-5}$ mol/L

The approximation is valid. The pH and pOH of the solution can be calculated by:

$pOH = -\log [OH^-] = - \log (1.8 \text{ x} 10^{-5}) = 4.74$

$pH = 14.00 - pOH = 14.00 - 4.74 = 9.26$

The pH of the solution is 9.26, indicating that it is an alkaline solution. For comparison, the pH of a 0.1 mol/L solution of NH_3 is 11.1, thus the alkalinity of the solution has decreased due to the addition of the NH_4^+ ion.

2. Calculate pK_a from K_a

Problem

Calculate pK_a for the following acids:

(a) HSO_4^-, $K_a = 1.2 \times 10^{-2}$

(b) HCN, $K_a = 4.0 \times 10^{-10}$

(c) phenol, C_6H_5OH, $K_a = 1.3 \times 10^{-10}$

Approach

$pK_a = -\log K_a$

Solution

(a) HSO_4^-: $pK_a = -\log(1.2 \times 10^{-2}) = 1.92$

(b) HCN: $pK_a = -\log(4.0 \times 10^{-10}) = 9.40$

(c) phenol, C_6H_5OH: $pK_a = -\log(1.3 \times 10^{-10}) = 9.89$

3. Using the Henderson-Hasselbalch Equation

Question

If 3.00 g of benzoic acid ($C_6H_5CO_2H$) and 2.00 g of sodium benzoate ($NaC_6H_5CO_2$) are dissolved in enough water to make 1.50 L of solution, what is the pH of this solution? $K_a = 6.3 \times 10^{-5}$ for benzoic acid.

Approach

First, calculate the pK_a of the acid. Then, calculate the concentrations of the benzoic acid and its conjugate base, benzoate ion. Finally, find the pH of the solution using the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Solution

The pK_a of sodium benzoate is:

$pK_a = -\log(6.3 \times 10^{-5}) = 4.20$

The concentrations of benzoic acid and benzoate ion from sodium benzoate are:

$$3.00\text{ g benzoic acid}\left(\frac{1\text{ mol}}{122.1\text{ g}}\right) = 0.0245\text{ mol benzoic acid}$$

$$2.00\text{ g sodium benzoate}\left(\frac{1\text{ mol}}{144.1\text{ g}}\right) = 0.0139\text{ mol sodium benzoate}$$

The solution is 1.50 L in volume, therefore the concentration of benzoic acid is:

$$\frac{0.0245 \text{ mol}}{1.50 \text{ L}} = 0.0164 \text{ mol/L}$$

Similarly, the concentration of sodium benzoate is 0.00927 mol/L. Using the Henderson-Hasselbalch equation, the pH is calculated by:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = 4.20 + \log \frac{0.00927}{0.0164} = 3.95$$

The pH of the solution is 3.95, which is lower than the $\text{p}K_a$ because the ratio of sodium benzoate to benzoic acid was less than 1.

4. Common Ion Effect: Preparing Buffers

Question

What ratio of $\frac{[CHO_2^-]}{[CHO_2H]}$ is needed to make a sodium formate-formic acid buffer solution having a pH of 4.80? $K_a = 1.77 \times 10^{-4}$ for formic acid, CHO_2H.

$$CHO_2H(aq) + H_2O(\ell) \rightleftharpoons H_3O^+ + CHO_2^-$$

Solution

A pH of 4.80 corresponds to $[H_3O^+] = 1.58 \times 10^{-5}$ mol/L. The ratio of acid to common ion in a buffer is given as:

$$[H_3O^+] = \frac{[CHO_2H]}{[CHO_2^-]} \times 1.77 \times 10^{-4} = 1.58 \times 10^{-5} \text{ mol/L}$$

$$\frac{[CHO_2^-]}{[CHO_2H]} = \frac{1.77 \times 10^{-4}}{1.58 \times 10^{-5}} = 11.2$$

Therefore, the $[CHO_2^-]/[CHO_2H]$ ratio must be 11.2 to 1 to attain a solution having a pH of 4.80 with this buffer system. For example, if 1 mol/L CHO_2 H is used, the solution must be 11.2 mol/L in sodium formate.

5. Titration of a Strong Acid by a Strong Base

Problem

Calculate the pH of a solution in which 10.0 mL of 0.100 mol/L NaOH is added to 20.0 mL of 0.100 mol/L HCl.

Approach

First, write the reaction for NaOH and HCl. Then, calculate the number of moles of each reactant. To find $[H^+]$, calculate the number of moles of excess H^+, and divide by the total volume of solution. Finally, calculate the pH from $[H^+]$.

Solution

These reactants are strong electrolytes, thus this problem is essentially one of stoichiometry. The reaction is:

$$H^+ + OH^- \longrightarrow H_2O(\ell)$$

Calculate the number of moles of each reactant by multiplying the volume (in liters) of each solution by its molar concentration.

Moles H^+ = 0.0200 L * 0.100 mol/L = 0.00200 mol

Moles OH^- = 0.0100 L * 0.100 mol/L = 0.00100 mol

Since all of the OH^- reacts, the excess H^+ = 0.00200 mol - 0.00100 mol = 0.00100 mol H^+. With this number, we can now calculate the concentration of H^+ by dividing this amount by the total volume of solution:

$$[H^+] = \frac{0.00100 \text{ mol } H^+}{0.0200 \text{ L} + 0.0100 \text{ L solution}} = 0.0333 \text{ mol/L } H^+$$

The pH of the solution is:

$$pH = -\log [H^+] = -\log (0.0333) = 1.48$$

6. Titration of Weak Acid by a Strong Base

Problem

Calculate the molar concentration of nicotinate ion at the equivalence point when 20. mL of 0.10 mol/L nicotoinic acid, $HC_6H_4NO_2$, is titrated with 0.10 mol/L sodium hydroxide, NaOH. $K_a = 1.4 \times 10^{-5}$ for nicotinic acid.

$$C_6H_4NO_2^- + H_2O(\ell) \rightleftharpoons HC_6H_4NO_2(aq) + OH^-$$

Approach

At the equivalence point, equal molar amounts of nicotinic acid and sodium hydroxide react to give a solution of sodium nicotinate. The molar amount of ion equals the initial amount of acid, therefore we can calculate the moles of nicotinate ion. We can then calculate the concentration of nicotinate ion by dividing the number of moles of nicotinate ion by the total solution volume.

Solution

Assuming the reaction is complete, 20. mL of 0.10 mol/L NaOH is needed to react with 20. mL of 0.10 mol/L nicotinic acid. The molar amount of nicotinate ion formed equals the initial amount of nicotinic acid:

$$\text{Moles of nicotinate ion} = \frac{0.020 \text{ L solution} \times 0.10 \text{ mol } C_6H_4NO_2^-}{1 \text{ L solution}} = 0.0020 \text{ mol } C_6H_4NO_2^-$$

The total volume of the solution is 40. mL assuming there is no loss in volume due to mixing. To find the molar concentration of nicotinate ion, divide the molar amount of nicotinate ion by the total solution volume:

$$\text{Molar concentration of nicotinate ion} = \frac{0.020 \text{ mol } C_6H_4NO_2^-}{0.040 \text{ L solution}} = 0.050 \text{ mol/L}$$

7. Titration of Weak Acid by a Strong Base

Question

Using the information in question 3, calculate the pH of the solution at the equivalence point.

Solution

The K_a for nicotinic acid is 1.4×10^{-5}, therefore K_b for nicotinate ion (the conjugate base) is:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-5}} = 7.1 \times 10^{-10}$$

Let x = $[OH^-]$.

	$HC_6H_4NO_2(aq)$ +	$OH^-(\ell) \rightleftarrows$	$C_6H_4NO_2^-$ +	$H_2O(aq)$
Initial	0.050	0	0	
Change	- x	+ x	+ x	
Equilibrium	0.050 - x	x	x	

Substituting into the equilibrium equation, gives

$$K_b = \frac{[HC_6H_4NO_2][OH^-]}{[C_6H_4NO_2^-]} = \frac{x^2}{0.050 - x}$$

$$\text{If } K_a < \frac{[\text{initial}]}{1000}, \text{ then } K_a = \frac{x^2}{[\text{initial}]} \times \cong \frac{x^2}{[\text{initial}]}$$

Assuming that (0.050-x) is approximately equal to 0.050,

$$K_b = \frac{[HC_6H_4NO_2][OH^-]}{[C_6H_4NO_2^-]} = \frac{x^2}{0.050} = 7.1 \times 10^{-10}$$

$[OH^-] = x = 6.0 \times 10^{-6}$

Note that x is very small compared to 0.050, so our assumption is valid. $[OH^-]$ is 6.0×10^{-6} mol/L. The pH can now be calculated:

$pH = 14.00 - pOH = 14.00 - (-\log [OH^-]) = 14.00 + \log (6.0 \times 10^{-6}) = 8.78$

The pH of the solution is **8.7**8. The solution pH of 8.78 is greater than 7, meaning it is basic. This is expected because the result of a reaction between a weak acid and a strong base is a weak base, and in this case, nicotinate ion.

CH 223 Chapter Fifteen Concept Guide

1. Solubility Product

Problem

The solubility of silver iodide, AgI, at 25 °C is 2.1×10^{-6} g/L. Calculate the solubility product of this salt from its solubility.

Approach

First, write the chemical equation, letting x represent the molar solubility. Then, write the equilibrium constant expression. Third, calculate the molar solubility from the solubility of AgI. Last, calculate the solubility product of AgI from the molar solubility calculated earlier.

Solution

Step 1. The chemical equation is:

$$\mathrm{AgI(s)} \rightleftarrows \underset{(x)}{\mathrm{Ag^{+}(aq)}} + \underset{(x)}{\mathrm{I^{-}(aq)}}$$

Step 2. The equilibrium constant expression is:

$K_{sp} = [Ag^{+}][I^{-}] = (x)(x) = x^{2}$

Step 3. Calculate the molar solubility from the solubility of AgI.

$$x = \left(\frac{2.1 \times 10^{-6}\ \mathrm{g\ AgI}}{1\ \mathrm{L}}\right)\left(\frac{1\ \mathrm{mol\ AgI}}{234.77\ \mathrm{g\ AgI}}\right) = 8.9 \times 10^{-9}\ \mathrm{mol/L}$$

Step 4. Calculate the solubility product of AgI from the molar solubility.

$K_{sp} = x^{2} = (8.9 \times 10^{-9})^{2} = 7.9 \times 10^{-17}$

2. Solubility Product

Problem

The solubility product of silver sulfate, Ag_2SO_4 is 1.5×10^{-5} at 25 °C. Calculate the solubility of this salt from its solubility product. Report the solubility in moles per liter and in grams per liter.

Approach

First, write the chemical equation, letting x represent the molar solubility. Then, write the equilibrium constant expression. Finally, solve the K_{sp} expression to find the solubility of Ag_2SO_4.

Solution

Step 1. The chemical equation is:

Step 2. The equilibrium constant expression is:

$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2x)^2(x) = 4x^3 = 1.5 \text{ x } 10^{-5}$

Step 3. Solve the K_{sp} expression to find the solubility of Ag_2SO_4.

$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2x)^2(x) = 4x^3 = 1.5 \text{ x } 10^{-5}$

x = 0.016 mol/L or 5.0 g/L

3. Solubility Product

Problem

The solubility product of $AlPO_4$ is $5.8 \text{ x } 10^{-19}$ at 25 °C. Calculate the solubility of this salt from its solubility product in moles per liter.

Approach

First, write the chemical equation, letting x represent the molar solubility. Then, write the equilibrium constant expression. Finally, solve the K_{sp} expression to find the solubility of $AlPO_4$.

Solution

Step 1. The chemical equation is:

Step 2. The equilibrium constant expression is:

$K_{sp} = [Al^{3+}][PO_4^{3-}] = (x)(x) = x^2 = 5.8 \text{ x } 10^{-19}$

Step 3. Solve the K_{sp} expression to find the solubility of $AlPO_4$.

$K_{sp} = [Ag^{3+}][PO_4^{3-}] = (x)(x) = x^2 = 5.8 \text{ x } 10^{-19}$

4. Ranking Solubilities

Question

Given the following information, which has a greater solubility: CuBr or CuCl?

$CuBr \quad K_{sp}$ at 25 °C = 5.2×10^{-9}

$CuCl \quad K_{sp}$ at 25 °C = 1.2×10^{-6}

Solution

The stoichiometries for these two salts are the same: 1:1. Thus, we can compare their K_{sp} values to determine which salt is more soluble. The larger the value of K_{sp}, the more soluble the salt. CuCl has, therefore, a greater solubility than CuBr.

5. Precipitation Reactions

Question

The concentration of chromate ion in an aqueous solution is 0.012 mol/L.

(a) Will the precipitation of silver chromate take place if a concentration of silver ion of 1×10^{-6} mol/L is introduced by adding solid silver nitrate to the solution?

(b) If the answer to (a) is "no," what concentration of silver ion would be necessary to begin precipitation? The K_{sp} value of Ag_2CrO_4 is 2.5×10^{-12}.

$$Ag_2CrO_4(s) \qquad 2\,Ag^+(aq) + CrO_4^{2-}(aq)$$

Solution

(a) The ion product for the reaction of Ag_2CrO_4 is:

$$Q = [Ag^+]^2[CrO_4^{2-}] = (1 \times 10^{-6}\ \text{mol/L})^2(0.012\ \text{mol/L}) = 1 \times 10^{-14}$$

$$Q < K_{sp}$$

Because Q is less than K_{sp}, the forward reaction is favored and no precipitate forms.

(b) Precipitation will begin when $Q = K_{sp}$. The $[Ag^+]$ at which this occurs is calculated by substituting $[CrO_4^{2-}]$ = 0.012 mol/L into the K_{sp} expression and solving for $[Ag^+]$.

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = 2.5 \times 10^{-12}$$

$$K_{sp} = [Ag^+]^2[0.012\ \text{mol/L}] = 2.5 \times 10^{-12}$$

$$[Ag^+] = 1.4 \times 10^{-5}\ \text{mol/L}$$

For precipitation of silver chromate to begin, $[Ag^+]$ must be 1.4×10^{-5} mol/L.

6. Precipitation Reactions

Question

Will a precipitate of $Mg(OH)_2$ form if 10. mL of 0.010 M NaOH is added to 1.000 L of 0.015 mol/L $MgCl_2$? Assume that the volume of resulting solution is 1.015 L. The K_{sp} value of $Mg(OH)_2$ is 7.1×10^{-12}.

Solution

The concentrations of the ions in the resulting solution are:

The ion product is:

$$Q = [Mg^{2+}][OH^-]^2 = (1.5 \times 10^{-2})(9.9 \times 10^{-5})^2 = 1.5 \times 10^{-10}$$

$$Q > K_{sp}$$

Because Q is greater than K_{sp}, a precipitate of $Mg(OH)_2$ will form.

7. Common Ion Effect

Problem

The solubility constant of Ag_2SO_4 is 1.5×10^{-5}. Calculate the solubility of this salt in an aqueous solution that contains 0.25 mol/L of Na_2SO_4. Is there a common ion effect seen here? Assume that none of the ions reacts appreciably with water for form H^+ or OH^-.

Approach

First, write the chemical equation, letting x represent the molar solubility. Then, write the equilibrium constant expression to calculate the solubility of the salt in pure water from the solubility product. Then, calculate the molar solubility in Na_2SO_4 by solving for x. Last, comment on the calculated molar solubility in Na_2SO_4 compared to the solubility of the salt.

Solution

Step 1. The chemical equation is:

Step 2. The equilibrium constant expression for the salt in pure water is:

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2x)^2(x) = 4x^3 = 1.5 \times 10^{-5}$$

Solve the K_{sp} expression to find the solubility of Ag_2SO_4 in pure water.

$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2x)^2(x) = 4x^3 = 1.5 \times 10^{-5}$

Step 3. In this example, there are two sources of SO_4^{2-} in the solution: the dissolved Ag_2SO_4 and the initial Na_2SO_4 in the solution. The equilibrium constant expression becomes:

$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2x)^2(0.25 + x) = 1.5 \times 10^{-5}$

Step 4. The K_{sp} is small relative to the 0.25 mol/L initial SO_4^{2-}, therefore, we can assume that (0.25 + x) is approximately 0.25. Solving for x,

The approximation is valid. The molar solubility is 0.0039 mol/L, thus the common ion effect has reduced the solubility from 0.016 mol/L for Ag_2SO_4 in pure water to 0.0039 mol/L in the Na_2SO_4 solution.

8. Solubility and pH

Question

A 0.015 mol sample of solid $Fe(OH)_3$ was added to 1.0 L of water, and a strong acid was added until the $Fe(OH)_3$ precipitate dissolved. At what pH was all of the $Fe(OH)_3(s)$ dissolved? Assume negligible volume change due to the addition of the acid. The K_{sp} for $Fe(OH)_3$ is 3×10^{-39}.

$Fe(OH)_3(s) \quad Fe^{3+}(aq) + 3\ OH^-(aq)$

Solution

When all of the $Fe(OH)_3$ dissolved, 0.015 mol of Fe^{3+} was present in 1.0 L of solution. The concentration of OH^- at the point when dissolution was complete may be found from the solubility product expression for $Fe(OH)_3$.

$K_{sp} = [Fe^{3+}][OH^-]^3 = 3 \times 10^{-39}$

To calculate the pH, use the formula for pOH, where pOH = - log[OH^-]. Then, calculate the pH from pOH.

$pOH = -\log[OH^-] = -\log(6 \times 10^{-13}) = 12.2$

$pH = 14.0 - pOH = 14.0 - 12.2 = 1.8$

When all of the solid $Fe(OH)_3$ dissolved, the pH of the solution was 1.8.

9. Solubility and pH

Question

A 0.020 mol sample of solid $Fe(OH)_2$ was added to 1.0 L of water, and a strong acid was added until the $Fe(OH)_2$ precipitate dissolved. At what pH was all of the $Fe(OH)_2(s)$ dissolved? Assume negligible volume change due to the addition of the acid. The K_{sp} for $Fe(OH)_2$ is $8 \text{ x } 10^{-16}$.

$Fe(OH)_2(s) \quad Fe^{2+}(aq) + 2\ OH^-(aq)$

Solution

When all of the $Fe(OH)_2$ dissolved, 0.020 mol of Fe^{2+} was present in 1.0 L of solution. The concentration of OH- at the point when dissolution was complete may be found from the solubility product expression for $Fe(OH)_2$.

$K_{sp} = [Fe^{2+}][OH^-]^2 = 8 \text{ x } 10^{-16}$

To calculate the pH, use the formula for pOH, where pOH = - log[OH$^-$]. Then, calculate the pH from pOH.

$pOH = - \log[OH^-] = - \log (2 \text{ x } 10^{-7}) = 6.7$

$pH = 14.0 - pOH = 14.0 - 6.7 = 7.3$

When all of the solid $Fe(OH)_2$ dissolved, the pH of the solution was 7.3.

10. Solubility and Complex Ion Formation

Question

$Zn(OH)_2$ precipitates from an acidic aqueous solution by the addition of OH^- ion to Zn^{2+} ion. There is the danger, however, of redissolving the $Zn(OH)_2$ by addition of too much OH^- ion because of the formation of the $[Zn(OH)_4]^{2-}$ complex ion.

(a) What is the pH at which the concentration of Zn^{2+} falls below $1 \text{ x } 10^{-4}$ mol/L due to precipitation of $Zn(OH)_2$?

(b) What is the pH at which the concentration of $[Zn(OH)_4]^{2-}$ increases above $1 \text{ x } 10^{-4}$ mol/L? The pH range between these points is that in which almost all of the Zn^{2+} is present as a solid. The K_{sp} for $Zn(OH)_2$ is $1.2 \text{ x } 10^{-17}$ and the K of formation (K_f) for $[Zn(OH)_4]^{2-}$ is $2 \text{ x } 10^{20}$.

$Zn(OH)_2(s) \quad Zn^{2+}(aq) + 2\ OH^-(aq) \quad K_{sp} = [Zn^{2+}]\ [OH^-]^2$

Solution

(a) The formation of $Zn(OH)_2$ becomes important as the pH increases. The OH^- ion concentration in equilibrium when the concentration of Zn^{2+} is $1 \text{ x } 10^{-4}$ mol/L is

$[OH^-] = 3 \text{ x } 10^{-7}$ mol/L

To calculate the pH, use the formula for pOH, where pOH = - log$[OH^-]$. Then, calculate the pH from pOH.

pOH = - log$[OH^-]$ = - log $(3 \text{ x } 10^{-7})$ = 6.5

pH = 14.0 - pOH = 14.0 - 6.5 = 7.5

The pH at which the concentration of Zn^{2+} falls below $1 \text{ x } 10^{-4}$ mol/L due to precipitation of $Zn(OH)_2$ is 7.5.

(b) The formation of $Zn(OH)_2$ becomes even more important as the pH increases from neutral to alkaline values. The solubility of Zn^{2+} may be described by the equilibrium between the precipitate and the complex ion.

The OH^- ion concentration in equilibrium with the concentration of $Zn(OH)_4^{2-}$ being $1 \text{ x } 10^{-4}$ mol/L is

$$[OH^{-1}]^2 = \frac{Zn(OH)_4{}^{2-}}{K_{sp}K_f} = \frac{1 \text{ x } 10^{-4}}{(1.2 \text{ x } 10^{-17})(2 \text{ x } 10^{20})} = 4 \text{ x } 10^{-8}$$

$[OH^-] = 2 \text{ x } 10^{-4}$ mol/L

To calculate the pH, use the formula for pOH, where pOH = - log$[OH^-]$. Then, calculate the pH from pOH.

pOH = - log$[OH^-]$ = - log $(2 \text{ x } 10^{-4})$ = 3.7

pH = 14.0 - pOH = 14.0 - 3.7 = 10.3

The pH at which the concentration of $[Zn(OH)_4]^{2-}$ increases above $1 \text{ x } 10^{-4}$ mol/L is 10.3. Therefore, the optimum precipitation of Zn^{2+} will result by controlling the pH of the solution between 7.5 and 10.3.

CH 223 Chapter Sixteen Concept Guide

1. Enthalpy

Question

$\Delta H°$ for the following reaction is positive. What does this mean in terms of the relative strengths of the bonds in the reactants and products?

$CH_3OH(\ell) + NH_3(g) \rightarrow CH_3NH_2(g) + H_2O(g)$

Solution

The fact that $\Delta H°$ is positive indicates that the bonds broken in the reactants are stronger than the bonds formed in the products. The reactants are thus more stable than the products, explaining why the reaction requires an input of thermal energy to occur.

2. Entropy

Problem

For each of the following processes, predict whether you would expect entropy to be greater for the reactants or for the products.

(a) $CO_2(g) \rightarrow CO_2(s)$

(b) $KCl(s) \rightarrow KCl(aq)$

(c) $MgCO_3(s) + \text{heat} \rightarrow MgO(s) + CO_2(g)$

Solution

(a) For a given compound, molecules in the vapor state have higher entropy because the vapor state is more disorder than is the solid state. The entropy of solid carbon dioxide is, therefore, less than of CO_2 vapor.

(b) Solid KCl is a more ordered state than KCl dissolved in water. Thus, the entropy of the dissolved KCl is greater than that of the solid KCl.

(c) One mole of solid $MgCO_3$ yields one mole of solid MgO and one mole of gaseous CO_2. As the number of moles increases from the reactant to the product side of the equation, the entropy also increases. This is particularly true when one of the products is a gas. The products, therefore, have a greater entropy than do the reactants.

3. Entropy in Physical Changes

Question

Would you predict an increase or decrease in the entropy for the system that undergoes the change described below?

(a) Making rock candy (crystalline sugar) from a saturated sugar solution. (System = candy + solution)

(b) Putting cream in your coffee (System = cream + coffee)

Solution

(a) The crystallization of the sugar would involve a decrease in entropy. The molecules are more ordered in a crystal than in a solution.

(b) Mixing the cream and the coffee would cause entropy to increase. The randomness of the combined liquids is greater than that of the liquids in separate containers.

4. Entropy in Physical Changes

Question

Calculate the standard state entropy change for the vaporization of one mole of argon at the normal boiling point. ΔH° is 6519 J/mol for argon at 87.5 K. Is this an increase or decrease in entropy?

Solution

The entropy change for this change of state is

$$\Delta S^\circ(87.5)(\text{vaporization}) = \frac{\Delta H^\circ(87.5)(\text{vaporization})}{T}$$

ΔS° is positive, indicating that the entropy of argon has increased by 74.5 J/(K mol).

5. Entropy in Chemical Reactions

Problem

Predict whether the entropy change for each of the following reactions will be large and negative, large and positive, or small:

(a) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$

(b) $2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$

(c) $2\ ZnS(s) + 3\ O_2(g) + \text{heat} \rightarrow 2\ ZnO(s) + 2\ SO_2(g)$

Solution

(a) Two moles of gas react to form two moles of gaseous product. Since the number of moles does not change, we would expect only a small change in randomness for this reaction. (The actual value is 20.07 J/K.)

(a) Two moles of gas react to form three moles of gaseous product. This net gain of one mole indicates that a large, positive value for $\Delta S°$ is likely. (The actual value is 148.54 J/K.)

(a) Two moles of a solid react with three moles of gas to produce two moles of a solid and two moles of gas. This is a net loss of one mole of gas, which represents a decrease in randomness. Thus, a large, negative value of $\Delta S°$ is expected. (The actual value is -147.1 J/K.)

6. ΔG° of Reaction

Problem

Calculate $\Delta G°$ for the following reaction and determine if it is spontaneous at 25 °C under standard state conditions. At this temperature, $\Delta H° = -91.34$ kJ and $\Delta S° = 41.5$ J/K for this reaction.

$CCl_4(\ell) + H_2(g) \rightarrow HCl(g) + CHCl_3(\ell)$

Solution

The value of $\Delta G°$ is

$$\Delta G° = \Delta H° - T\,\Delta S°$$

$$\Delta G° = (-91.34 \text{ kJ}) - (298.15)(41.5 \text{ J/K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$\Delta G° = -103.7 \text{ kJ}$$

The negative value of $\Delta G°$ indicates that the reaction will be spontaneous at this temperature under standard state conditions.

7. ΔG° of Reaction

Problem

Calculate $\Delta G°$ for the following reaction and determine if it is spontaneous at 25 °C. At this temperature, $\Delta H° = -391.9$ kJ and $\Delta S° = 10.29$ J/K for this reaction.

$O_3(g) + O(g) \rightarrow 2\, O_2(g)$

Solution

$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$

$$\Delta G^\circ = (-391.9\ \text{kJ}) - (298.15)(10.29\ \text{J/K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$\Delta G^\circ = -395.0\ \text{kJ}$$

The negative value of ΔG° indicates that the reaction will be spontaneous at this temperature.

8. Free Energy and Equilibrium

Problem

Calculate the equilibrium constant for the reaction shown in problem 1.

$CCl_4(\ell) + H_2(g) \rightarrow HCl(g) + CHCl_3(\ell)$

ΔG° is -103.7 kJ at 25 °C for this reaction.

Solution

The following equation shows the relationship between ΔG° and the equilibrium constant, K.

$\Delta G^\circ = -RT \ln K$, where R = 8.314 J/(K mol)

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{(-103.7\ \text{kJ})\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right)}{(8.314\ \text{J/K}\cdot\text{mol})(298\ \text{K})} = 41.86$$

$K = 1.5 \times 10^{18}$

Under standard state conditions at 25 °C, this reaction is spontaneous and the products are highly favored over the reactants at equilibrium.

CH 223 Chapter Seventeen Concept Guide

1. Half Reactions

Question

What are the half reactions for the reduction of iron(III) ion to iron(II) ion by tin(II) ion?

$Sn^{2+} + 2\ Fe^{3+} \rightarrow 2\ Fe^{2+} + Sn^{4+}$

Solution

Each iron(III) gains one electron during reduction and each tin(II) ion loses two electrons during oxidation.

Reduction half-reaction: $Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$

Oxidation half-reaction: $Sn^{2+}(aq) \rightarrow Sn^{4+} + 2e^{-}(aq)$

2. Ion-Electron Equations

Problem

Write the balanced half-reaction equation for the reduction of NO_3^- to $HNO_2(aq)$ in acidic solution.

Solution

Nitrate ion is reduced to nitrous acid: $NO_3^- \rightarrow HNO_2$

This equation is balanced with respect to the N atoms, but the oxygen atoms are unbalanced. Add one H_2O molecule to the products side to obtain

$NO_3^- \rightarrow HNO_2 + H_2O$

The H atoms are balanced in acidic solution by adding three H^+ atoms to the reactants side, giving

$3\ H^+ + NO_3^- \rightarrow HNO_2 + H_2O$

The charge is balanced by adding two e^- to the reactants side.

$3\ H^+ + NO_3^- + 2\ e^- \rightarrow HNO_2 + H_2O$

The total charge on the left is zero [(-1) + (3)(+1) + (2)(-1) = 0] and the total charge on the right is zero. The equation is balanced.

3. Cell Reactions

Problem

For a particular reaction, the anode, cathode, and overall cell reactions are:

$2\ H^+ + 2\ e^- \rightarrow H_2(g)$

$Mg(s) \rightarrow Mg^{2+} + 2\ e^-$

$Mg(s) + 2\ H^+ \rightarrow Mg^{2+} + H_2(g)$

Label each reaction as the anode, cathode, and cell reaction.

Solution

The anode is the site of an oxidation reaction. The cathode is the site of a reduction reaction. The cell reaction is the result of the anode reaction added to the cathode reaction.

Cathode Reaction: $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$

Anode Reaction: $Mg(s) \rightarrow Mg^{2+}(aq) + 2\ e^-$

Cell Reaction: $Mg(s) + 2\ H^+ \rightarrow Mg^{2+}(aq) + H_2(g)$

4. Electrochemical Cells

Question

A galvanic cell is prepared by immersing a strip of magnesium metal into 1 M $Mg(NO_3)_2$ and a strip of copper metal into 1 M $CuSO_4$. The two solutions are separated by an unglazed porcelain wall.

(a) Write the anode reaction.

(b) Write the cathode reaction.

(c) Write the net cell reaction.

(d) From which electrode do the electrons flow to the other electrode if a wire is used to connect the two electrodes?

(e) What is the standard voltage of this cell (in Volts)?

Solution

(a) $Mg(s) \rightarrow Mg^{2+}(aq) + 2\ e^-$

(b) $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$

(c) $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$

(d) The electrons flow from the magnesium electrode to the copper electrode if a wire connects the two electrodes.

(e) The voltage of this cell is 2.71 and is calculated by adding together the standard reduction potentials for the anode and cathode reaction.

$$\begin{array}{ll}
\mathrm{Mg(s)} \longrightarrow \mathrm{Mg^{2+}(aq)} + 2\,\mathrm{e^-} & -(-2.37) \\
\mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu(s)} & 0.34 \\
\hline
\mathrm{Mg(s)} + \mathrm{Cu^{2+}(aq)} \longrightarrow \mathrm{Mg^{2+}(aq)} + \mathrm{Cu(s)} & \text{Cell Voltage} = 2.71
\end{array}$$

5. Thermodynamics of Electrochemical Cells

Question

What is the standard cell potential for an electrochemical cell in which the following spontaneous reaction takes place? ΔG° for this reaction is - 50.61 kJ.

$Cl_2(g) + 2\ Br^-(aq) \rightarrow Br_2(aq) + 2\ Cl^-(aq)$

Solution

To solve for E°, we need to use

$$E^\circ = \frac{-\Delta G^\circ}{nF}$$

Before solving for E°, we must find the value of *n*, the moles of electrons being transferred, by writing the half-reactions for the reduction of Cl_2 and oxidation of Br^-.

$$\begin{array}{l}
\mathrm{Cl_2(g)} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cl^-(aq)} \\
2\,\mathrm{Br^-(aq)} \longrightarrow \mathrm{Br_2(aq)} + 2\,\mathrm{e^-} \\
\hline
\mathrm{Cl_2(g)} + 2\,\mathrm{Br^-(aq)} \longrightarrow \mathrm{Br_2(aq)}\ \ 2\,\mathrm{Cl^-(aq)}
\end{array}$$

The value of *n* is 2.

The cell potential is found by solving for E° and substituting *n* = 2 and the known value of ΔG°.

$E^\circ = -(-50.61\ kJ)/(2\ mole\ e^-)(96.5\ kJ/V\ mol\ e^-) = 0.262\ V$

6. Thermodynamics of Electrochemical Cells

Question

Under standard state conditions, the following reaction is spontaneous, and E° is 0.019 V.

$3\ Zn(s) + 2\ Cr^{3+}(aq) \rightarrow 3\ Zn^{2+}(aq) + 2\ Cr(s)$

Will this reaction occur spontaneously if $[Cr^{3+}] = 0.010$ mol/L and $[Zn^{2+}] = 5.5$ mol/L?

Solution

We will need to find the value of the reaction quotient and then solve for E.

$$Q = \frac{[Zn^{2+}]^3}{[Cr^{3+}]^2} = \frac{(5.5)^3}{(0.010)^2} = 1.7 \times 10^6$$

$$E = E^\circ - \left(\frac{0.0592}{n}\right)(\log Q) = 0.019 - \left(\frac{0.0592}{6}\right)\left(\log 1.7 \times 10^6\right)$$

$$E = -0.042$$

The negative cell potential implies that the reaction will not be spontaneous under these conditions. From Le Chatelier's principle, the reverse reaction would be expected to be favored.

7. Using the Faraday Constant

Question

A current of 1.65 amps is passed through a solution containing silver ions, Ag^+, for 10.0 minutes. The process causes silver to be deposited at the cathode. What mass of silver is deposited?

Solution

Step 1. Calculate the charge (number of coulombs) passed in 10.0 minutes.

Charge (Coulombs, C) = current (amps) x time (seconds)

$$\text{Charge (Coulombs, C)} = (1.65 \text{ amps})(10.0 \text{ minutes})\left(\frac{60 \text{ seconds}}{1 \text{ minute}}\right) = 990 \text{ C}$$

Step 2. Calculate the number of moles of electrons.

$$(990 \text{ C})\left(\frac{1 \text{ mole e}^-}{9.65 \times 10^4 \text{ C}}\right) = 1.03 \times 10^{-2} \text{ mol e}^-$$

Step 3. Calculate the number of moles of silver and then the mass of silver deposited.

$$\left(1.03 \times 10^{-2} \text{ mol e}^-\right)\left(\frac{1 \text{ mol Ag}}{1 \text{ mole e}^-}\right)\left(\frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}}\right) = 1.11 \text{ g Ag}$$

8. Using the Faraday Constant

Question

A current of 2.00 amps is passed through a solution of $Ni(NO_3)_2$ for 2.00 hours. What mass of nickel is deposited at the cathode?

Solution

Step 1. Calculate the charge (number of coulombs) passed in 2 hours.

Charge (Coulombs, C) = current (amps) x time (seconds)

$$\text{Charge (Coulombs, C)} = (2.00\ \text{amps})(2.00\ \text{hours})\left(\frac{60\ \text{minutes}}{1\ \text{hour}}\right)\left(\frac{60\ \text{seconds}}{1\ \text{minute}}\right) = 1.44 \times 10^4\ \text{C}$$

Charge = 1.44×10^4 C

Step 2. Calculate the number of moles of electrons.

$$\left(1.44 \times 10^4\ \text{C}\right)\left(\frac{1\ \text{mole e}^-}{9.65 \times 10^4\ \text{C}}\right) = 0.149\ \text{mol e}^-$$

Step 3. Calculate the number of moles of nickel and then the mass of nickel deposited.

$$\left(0.149\ \text{mol e}^-\right)\left(\frac{1\ \text{mol Ni}}{2\ \text{mole e}^-}\right)\left(\frac{58.693\,\text{g Ni}}{1\ \text{mol Ni}}\right) = 4.37\,\text{g Ni}$$

9. Batteries

Question

In this lesson, the anode, cathode, and net reactions for dry cell and alkaline batteries are shown. Based on these reactions, what is a possible disadvantage to a dry cell battery compared to alkaline battery?

Solution

In the dry cell battery, the products of the cathode reaction are gases. If current is drawn from the battery rapidly, the gaseous products cannot be consumed rapidly enough, resulting in a drop in potential. In the alkaline battery, no gases are formed, thus there is no decline in potential under high current loads.

10. Batteries

Problem

In principle, a battery can be made from aluminum metal and chlorine gas. Write a balanced equation for the reaction that occurs in a battery using Al^{3+}(aq)/Al(s) and Cl_2(g)/Cl^-(aq) half-reactions, and indicate which half-reaction occurs at the anode and which at the cathode.

Solution

$$2\ Al(s) + 3\ Cl_2(g) \rightarrow 2\ Al^{3+}(aq) + 6\ Cl^-(aq)$$

Al is the anode and the Cl_2/Cl^- compartment is the cathode.

11. Corrosion

Problem

A 5.0-kg magnesium bar is attached to a buried iron pipe to protect the pipe from corrosion. Explain how the magnesium protects the pipe.

Solution

E° for magnesium oxidation is 2.37 V. E° for iron oxidation is only 0.44 V. Magnesium is the better oxidizing agent, and thus protects the iron pipe because the metal oxidizes more readily than iron. It is a sacrificial reductant.

CH 223 Practice Problem Set #1

This is a ***practice problem set*** *and not the actual graded problem set that you will turn in for credit.*
Answers to each problem can be found at the end of this assignment.

Covering: **Chapter Thirteen** *and* **Chapter Guide One**
Important Tables and/or Constants: **R = 0.082057 L atm mol^{-1} K^{-1}, 760 mm Hg = 1 atm**

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1. Write equilibrium constant expressions for the following reactions. For gases use either pressures or concentrations.
   a. $2\ H_2O_2(g) \rightleftharpoons 2\ H_2O(g) + O_2(g)$
   b. $CO(g) + {}^1/_2\ O_2(g) \rightleftharpoons CO_2(g)$
   c. $C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$
   d. $NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g)$
2. $K = 5.6 \times 10^{-12}$ at 500 K for the dissociation of iodine molecules to iodine atoms.
   $$I_2(g) \rightleftharpoons 2\ I(g)$$
   A mixture has $[I_2] = 0.020$ mol/L and $[I] = 2.0 \times 10^{-8}$ mol/L. Is the reaction at equilibrium (at 500 K)? If not, which way must the reaction proceed to reach equilibrium?
3. The reaction
   $$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
   was examined at 250 °C. At equilibrium, $[PCl_5] = 4.2 \times 10^{-5}$ mol/L, $[PCl3] = 1.3 \times 10^{-2}$ mol/L, and $[Cl_2] = 3.9 \times 10^{-3}$ mol/L. Calculate K for the reaction.
4. The value of K for the interconversion of butane and isobutane is 2.5 at 25 °C.
   $$\text{butane}(g) \rightleftharpoons \text{isobutane}(g)$$
   If you place 0.017 mol of butane in a 0.50 L flask at 25 °C and allow equilibrium to be established, what will be the equilibrium concentrations of the two forms of butane?
5. The equilibrium constant for the dissociation of iodine molecules to iodine atoms
   $$I_2(g) \rightleftharpoons 2\ I(g)$$
   is 3.76×10^{-3} at 1000 K. Suppose 0.105 mol of I_2 is placed in a 12.3 L flask at 1000 K. What are the concentrations of I_2 and I when the system comes to equilibrium?
6. Dinitrogen trioxide decomposes to NO and NO_2 in an endothermic process ($\Delta H = 40.5$ kJ/mol).
   $$N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$$
   Predict the effect of the following changes on the position of the equilibrium; that is, state which way the equilibrium will shift (left, right, or no change) when each of the following changes is made.
   a. adding more $N_2O_3(g)$
   b. adding more $NO_2(g)$
   c. increasing the volume of the reaction flask
   d. lowering the temperature
7. Consider the isomerization of butane with an equilibrium constant of $K = 2.5$ (see question #4, above.) The system is originally at equilibrium with [butane] = 1.0 M and [isobutane] = 2.5 M.
   a. If 0.50 mol/L of isobutane is suddenly added and the system shifts to a new equilibrium position, what is the equilibrium concentration of each gas?
   b. If 0.50 mol/L of butane is added and the system shifts to a new equilibrium position, what is the equilibrium concentration of each gas?

8. Which of the following correctly relates the equilibrium constants for the two reactions shown?

$$A + B \rightleftharpoons 2C \qquad K_1$$

$$C \rightleftharpoons {}^1/_2\,A + {}^1/_2\,B \qquad K_2$$

a. $K_2 = 1/(K_1)^{1/2}$ c. $K_2 = K_1^2$

b. $K_2 = 1/K_1$ d. $K_2 = -K_1^{1/2}$

9. Calculate K for the reaction

$$SnO_2(s) + 2\ CO(g) \rightleftharpoons Sn(s) + 2\ CO_2(g)$$

given the following information:

$$SnO_2(s) + 2\ H_2(g) \rightleftharpoons Sn(s) + 2\ H_2O(g) \qquad K = 8.12$$

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad K = 0.771$$

10. Ammonium hydrogen sulfide decomposes on heating. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ If K_p for this reaction is 0.11 at 25 °C (when the partial pressures are measured in atmospheres), what is the total pressure in the flask at equilibrium?

11. Sulfuryl chloride, SO_2Cl_2, is a compound with very irritating vapors; it is used as a reagent in the synthesis of organic compounds. When heated to a sufficiently high temperature it decomposes to SO_2 and Cl_2.

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g) \qquad K = 0.045 \text{ at } 375\ °C$$

a. Suppose 6.70 g of SO_2Cl_2 is placed in a 1.00 L flask and then heated to 375 °C. What is the concentration of each of the compounds in the system when equilibrium is achieved? What fraction of SO_2Cl_2 has dissociated?

b. What are the concentrations of SO_2Cl_2, SO_2, and Cl_2 at equilibrium in the 1.00 L flask at 375 °C if you begin with a mixture of SO_2Cl_2 (6.70 g) and Cl_2 (1.00 atm)? What fraction of SO_2Cl_2 has dissociated?

c. Compare the fractions of SO_2Cl_2 in parts (a) and (b). Do they agree with your expectations based on Le Chatelier's principle?

12. Neither $PbCl_2$ nor PbF_2 is appreciably soluble in water. If solid $PbCl_2$ and solid PbF_2 are placed in equal amounts of water in separate beakers, in which beaker is the concentration of Pb^{2+} greater? Equilibrium constants for these solids dissolving in water are as follows:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq) \qquad K = 1.7 \times 10^{-5}$$

$$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ F^-(aq) \qquad K = 3.7 \times 10^{-8}$$

13. Characterize each of the following as product- or reactant- favored.

a. $CO(g) + {}^1/_2\,O_2(g) \rightleftharpoons CO_2(g) \qquad K_p = 1.2 \times 10^{45}$

b. $H_2O(g) \rightleftharpoons H_2(g) + {}^1/_2\,O_2(g) \qquad K_p = 9.1 \times 10^{-41}$

c. $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad K_p = 6.5 \times 10^{11}$

14. The reaction of hydrogen and iodine to give hydrogen iodide has an equilibrium constant, K_c, of 56 at 435 °C.

a. What is the value of K_p?

b. Suppose you mix 0.45 mol of H_2 and 0.45 mol of I_2 in a 10.0 L flask at 435 °C. What is the total pressure of the mixture before and after equilibrium is achieved?

c. What is the partial pressure of each gas at equilibrium?

Answers to the Practice Problem Set:

1. *Answers:*

   a. $K = \frac{[H_2O]^2[O_2]}{[H_2O_2]^2}$ $K_p = \frac{P^2_{H_2O}P_{O_2}}{P^2_{H_2O_2}}$

   b. $K = \frac{[CO_2]}{[CO][O_2]^{1/2}}$ $K_p = \frac{P_{CO_2}}{P_{CO}P^{1/2}_{O_2}}$

   c. $K = \frac{[CO]^2}{[CO_2]}$ $K_p = \frac{P^2_{CO}}{P_{CO_2}}$

   d. $K = \frac{[CO_2]}{[CO]}$ $K_p = \frac{P_{CO_2}}{P_{CO}}$
2. No, Q = 2.0×10^{-14}, and Q < K, so to the right (more products)
3. $K = 1.2$
4. [isobutane] = 0.024 M, and [butane] = 0.010 M
5. $[I_2] = 0.00614$ and $[I] = 0.00480$ M
6. a. right b. left c. right d. left
7. a. [butane] = 1.1 M, [isobutane] = 2.9 M; b. [butane] = 1.1 M, [isobutane] = 2.9 M
8. equation (a)
9. 13.7
10. 0.66 atm
11. a. $[SO_2Cl_2] = 0.020$ M, $[SO_2] = [Cl_2] = 0.030$ M, and fraction = 0.60 b. $[SO_2Cl_2] = 0.025$ M, $[SO_2] = 0.025$ M, $[Cl_2] = 0.044$ M, and fraction = 0.50 c. Yes, Le Chatelier's principle predicts equilibrium moves to the reactant side, confirmed
12. $PbCl_2$
13. a. product favored b. reactant favored c. product favored
14. a. $K_p = 56$ b. *before:* 5.2 atm *after:* 5.2 atm c. $P_{H2} = P_{I2} = 0.55$ atm, $P_{HI} = 4.1$ atm

CH 223 Practice Problem Set #2

This is a ***practice problem set*** *and not the actual graded problem set that you will turn in for credit.*
Answers to each problem can be found at the end of this assignment.

Covering: **Chapter Fourteen Part I** *and* **Chapter Guide Two**

Important Tables and/or Constants: The **Table of Acids and Bases for CH 223** *which follows problem set #2, and* **K_w = 1.00 x 10^{-14}** at 25 °C

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1. What are the products of each of the following acid–base reactions? Indicate the acid and its conjugate base, and the base and its conjugate acid.
   a. $HNO_3 + H_2O \rightarrow$
   b. $HSO_4^{-1} + H_2O \rightarrow$
   c. $H_3O^+ + F^{-1} \rightarrow$
2. Write balanced equations showing how the hydrogen oxalate ion, $HC_2O_4^{-1}$, can be both a Brønsted acid and a Brønsted base.
3. In each of the following acid–base reactions, identify the Brønsted acid and base on the left and their conjugate partners on the right.
   a. $C_5H_5N(aq) + CH_3CO_2H(aq) \rightleftharpoons C_5H_5NH^+(aq) + CH_3CO_2^-(aq)$
   b. $N_2H_4(aq) + HSO_4^-(aq) \rightleftharpoons N_2H_5^+(aq) + SO_4^{2-}(aq)$
   c. $[Al(H_2O)_6]^{3+}(aq) + OH^-(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_2O(l)$
4. An aqueous solution has a pH of 3.75. What is the hydronium ion concentration of the solution? What is the hydroxide ion concentration of the solution? Is it acidic or basic?
5. What is the pH of a 0.0015 M solution of $Ba(OH)_2$?
6. Several acids are listed here with their respective equilibrium constants:

$$C_6H_5OH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^{-1}(aq)$$
$$K_a = 1.3 \times 10^{-10}$$
$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^{-1}(aq)$$
$$K_a = 1.8 \times 10^{-4}$$
$$HC_2O_4^{-1}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2O_4^{2-}(aq)$$
$$K_a = 6.4 \times 10^{-5}$$

   a. Which is the strongest acid? Which is the weakest acid?
   b. Which acid has the weakest conjugate base?
   c. Which acid has the strongest conjugate base?
7. Epinephrine hydrochloride has a pK_a value of 9.53. What is the value of K_a?
8. A weak base has $K_b = 4.7 \times 10^{-11}$. What is the value of K_a for the conjugate acid?
9. Which is the stronger of the following two acids?
   a. acetic acid, CH_3CO_2H, $K_a = 1.8 \times 10^{-5}$
   b. chloroacetic acid, $ClCH_2CO_2H$, $pK_a = 2.87$
10. Equal molar quantities of sodium hydroxide and sodium hydrogen phosphate (Na_2HPO_4) are mixed.
    a. Write the balanced, net ionic equation for the acid–base reaction that can, in principle, occur.
    b. Does the equilibrium lie to the right or left?
11. A 0.015 M solution of hydrogen cyanate, HOCN, has a pH of 2.67.
    a. What is the hydronium ion concentration in the solution?

   b. What is the ionization constant, K_a, for the acid?

12. A 0.015 M solution of a base has a pH of 10.09.
    a. What are the hydronium and hydroxide ion concentrations of this solution?
    b. What is the value of K_b for this base?
13. Phenol (C_6H_5OH), commonly called carbolic acid, is a weak organic acid.

$$C_6H_5OH(aq) + H_2O(l) \rightleftharpoons C_6H_5O^{-1}(aq) + H_3O^{+}(aq) \quad K_a = 1.3 \times 10^{-10}$$

    If you dissolve 0.195 g of the acid in enough water to make 125 mL of solution, what is the equilibrium hydronium ion concentration? What is the pH of the solution?

14. Calculate the pH of a 0.12 M aqueous solution of the base aniline, $C_6H_5NH_2$ (The K_b for aniline equals 4.0 x 10^{-10}).

$$C_6H_5NH_2(aq) + H_2O\ (l) \rightleftharpoons C_6H_5NH_3^{+1}(aq) + OH^{-1}(aq)$$

15. Calculate the hydronium ion concentration and pH in a 0.20 M solution of ammonium chloride, NH_4Cl.
16. Decide whether each of the following substances should be classified as a Lewis acid or a Lewis base.
    a. H_2NOH in the reaction: $H_2NOH(aq) + HCl(aq) \rightarrow [H_3NOH][Cl](aq)$
    b. $Fe^{2+}(aq)$
    c. CH_3NH_2
17. Given the following solutions:
    a. 0.1 M NH_3
    b. 0.1 M Na_2CO_3
    c. 0.1 M NaCl
    d. 0.1 M CH_3CO_2H
    e. 0.1 M NH_4Cl
    f. 0.1 M $NaCH_3CO_2$
    g. 0.1 M $NH_4CH_3CO_2$
    i. Which of the solutions are acidic?
    ii. Which of the solutions are basic?
    iii. Which of the solutions is most acidic?
18. The equilibrium constant for the reaction of formic acid and sodium hydroxide is 1.8 x 10^{10}. Confirm this value.

Answers to the Practice Problem Set:

1. *Answers:*
   a. HNO_3 + H_2O → H_3O^+ + NO_3^-
   acid A base B conjugate acid of B conjugate base of A
   b. HSO_4^- + H_2O → H_3O^+ + SO_4^{2-}
   acid A base B conjugate acid of B conjugate base of A
   c. H_3O^+ +F^- → HF + H_2O
   acid A base B conjugate acid of B conjugate base of A
2. *Answers:*
   Brønsted acid: $HC_2O_4^-(aq) + H_2O(\ell) \rightleftarrows H_3O^+(aq) + C_2O_4^{2-}(aq)$
   Brønsted base: $HC_2O_4^-(aq) + H_2O(\ell) \rightleftarrows H_2C_2O_4(aq) + OH^-(aq)$
3. *Answers:*

	Brønsted acid	Brønsted base	conjugate base	conjugate acid
a.	CH_3CO_2H	C_5H_5N	$CH_3CO_2^-$	$C_5H_5NH^+$
b.	HSO_4^-	N_2H_4	SO_4^{2-}	$N_2H_5^+$
c.	$[Al(H_2O)_6]^{3+}$	OH^-	$[Al(H_2O)_5(OH)]^{2+}$	H_2O

4. $[H_3O^+] = 1.8 \times 10^{-4}$ M; $[OH^-] = 5.6 \times 10^{-11}$ M; acidic
5. pH = 11.48
6. a. HCO_2H; weakest acid = C_6H_5OH b. HCO_2H c. C_6H_5OH
7. 3.0×10^{-10}
8. 2.1×10^{-4}
9. chloroacetic acid
10. a. $OH^-(aq) + HPO_4^{2-}(aq) \rightleftarrows H_2O(\ell) + PO_4^{3-}(aq)$ b. right
11. a. 0.0021 M b. $3.6 \text{ x } 10^{-4}$
12. $[H_3O^+] = 8.1 \times 10^{-11}$ M; $[OH^-] = 1.2 \times 10^{-4}$ M b. $9.7 \text{ x } 10^{-7}$
13. $[H_3O^+] = 1.5 \times 10^{-6}$ M; pH = 5.83
14. pH = 8.84
15. $[H_3O^+] = 1.1 \times 10^{-5}$ M; pH = 4.98
16. a. Lewis base b. Lewis acid c. Lewis base
17. a. CH_3CO_2H and NH_4Cl b. NH_3, Na_2CO_3, and $NaCH_3CO_2$ c. CH_3CO_2H
18. *Answers:*
    $HCO_2H(aq) + H_2O(\ell) \rightleftarrows HCO_2^-(aq) + H_3O^+(aq)$ $K_a = 1.8 \times 10^{-4}$
    $OH^-(aq) + H_3O^+(aq) \rightleftarrows 2\ H_2O(\ell)$ $K = 1/K_w$
    $HCO_2H(aq) + OH^-(aq) \rightleftarrows H_2O(\ell) + HCO_2^-(aq)$ $K = (1.8 \times 10^{-4})/K_w = 1.8 \times 10^{10}$

CH 223 Practice Problem Set #3

This is a ***practice problem set*** *and not the actual graded problem set that you will turn in for credit.*
Answers to each problem can be found at the end of this assignment.

Covering: **Chapter Fourteen Part II** *and* **Chapter Guide Three**

Important Tables and/or Constants: "**Titration Guide**" *(Handout),* "**Buffers and Henderson-Hasselbalch Guide**" *(Handout)* and the **Table of Acids and Bases for CH 223** *(in problem set #3),* **K_w = 1.00 x 10^{-14}** at 25 °C

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1. Calculate the hydronium ion concentration and pH of the solution that results when 22.0 mL of 0.15 M acetic acid, CH_3CO_2H, is mixed with 22.0 mL of 0.15 M NaOH.
2. For each of the following cases, decide whether the pH is less than 7, equal to 7, or greater than 7.
   a. equal volumes of 0.10 M acetic acid, CH_3CO_2H, and 0.10 M KOH are mixed
   b. 25 mL of 0.015 M NH_3 is mixed with 25 mL of 0.015 M HCl
   c. 150 mL of 0.20 M HNO_3 is mixed with 75 mL of 0.40 M NaOH
3. Does the pH of the solution increase, decrease, or stay the same when you
   a. Add solid ammonium chloride to a dilute aqueous solution of NH_3?
   b. Add solid sodium acetate to a dilute aqueous solution of acetic acid?
   c. Add solid NaCl to a dilute aqueous solution of NaOH?
4. What is the pH of a solution that consists of 0.20 M ammonia, NH_3, and 0.20 M ammonium chloride, NH_4Cl?
5. What is the pH of the solution that results from adding 30.0 mL of 0.015 M KOH to 50.0 mL of 0.015 M benzoic acid?
6. What mass of sodium acetate, $NaCH_3CO_2$, must be added to 1.00 L of 0.10 M acetic acid to give a solution with a pH of 4.50?
7. What is the pH of the buffer solution that contains 2.2 g of NH_4Cl in 250 mL of 0.12 M NH_3? Is the final pH lower or higher than the pH of the original ammonia solution?
8. A buffer is composed of formic acid and its conjugate base, the formate ion.
   a. What is the pH of a solution that has a formic acid concentration of 0.050 M and a sodium formate concentration of 0.035 M?
   b. What must the ratio of acid to conjugate base be to increase the pH by 0.5 unit?
9. Calculate the pH of a solution that has an acetic acid concentration of 0.050 M and a sodium acetate concentration of 0.075 M.
10. Which of the following combinations would be the best to buffer the pH of a solution at approximately 9?
    a. HCl and NaCl
    b. NH_3 and NH_4Cl
    c. CH_3CO_2H and $NaCH_3CO_2$
11. Describe how to prepare a buffer solution from NaH_2PO_4 and Na_2HPO_4 to have a pH of 7.5.
12. A buffer solution was prepared by adding 4.95 g of sodium acetate, $NaCH_3CO_2$, to 2.50 x 10^2 mL of 0.150 M acetic acid, CH_3CO_2H.
    a. What is the pH of the buffer?
    b. What is the pH of 1.00 x 10^2 mL of the buffer solution if you add 82 mg of NaOH to the solution?

13. A buffer solution is prepared by adding 0.125 mol of ammonium chloride to 5.00 x 102 mL of 0.500 M solution of ammonia.
    a. What is the pH of the buffer?
    b. If 0.0100 mol of HCl gas is bubbled into 5.00 x 10^2 mL of the buffer, what is the new pH of the solution?
14. Phenol, C_6H_5OH, is a weak organic acid. Suppose 0.515 g of the compound is dissolved in exactly 125 mL of water. The resulting solution is titrated with 0.123 M NaOH.

    $$C_6H_5OH(aq) + OH^-(aq) \rightleftarrows C_6H_5O^{-1}(aq) + H_2O(l)$$

    a. What is the pH of the original solution of phenol?
    b. What are the concentrations of all of the following ions at the equivalence point: Na^+, H_3O^+, OH^-, and $C_6H_5O^{-1}$?
    c. What is the pH of the solution at the equivalence point?
15. You require 36.78 mL of 0.0105 M HCl to reach the equivalence point in the titration of 25.0 mL of aqueous ammonia.
    a. What was the concentration of NH_3 in the original ammonia solution?
    b. What are the concentrations of H_3O^+, OH^{-1}, and NH_4^+ at the equivalence point?
    c. What is the pH of the solution at the equivalence point?
16. For the titration of 50.0 mL of 0.150 M ethylamine, $C_2H_5NH_2$, with 0.100 M HCl, find the pH at each of the following points and then use that information to sketch the titration curve and decide on an appropriate indicator.
    a. at the beginning, before HCl is added
    b. at the halfway point in the titration
    c. when 75% of the required acid has been added
    d. at the equivalence point
    e. when 10.0 mL more HCl has been added than is required
    f. Sketch the titration curve.
    g. Suggest an appropriate indicator for this titration.
17. You titrate 25.0 mL of 0.10 M NH3 with 0.10 M HCl.
    a. What is the pH of the NH3 solution before the titration begins?
    b. What is the pH at the equivalence point?
    c. What is the pH at the halfway point of the titration?
    d. What indicator in Figure 18.10 could be used to detect the equivalence point?
    e. Calculate the pH of the solution after adding 5.00, 15.0, 20.0, 22.0, and 30.0 mL of the acid. Combine this information with that in parts (a)–(c) and plot the titration curve.
18. Aniline hydrochloride, $(C_6H_5NH_3)Cl$, is a weak acid with a conjugate base aniline ($C_6H_5NH_2$). The acid can be titrated with a strong base such as NaOH. Assume 50.0 mL of 0.100 M aniline hydrochloride is titrated with 0.185 M NaOH (K_a for aniline hydrochloride is 2.4 x 10^{-5}.) The equation: $C_6H_5NH_3^+(aq) + OH^-(aq) \rightleftarrows C_6H_5NH_2(aq) + H_2O(\ell)$
    a. What is the pH of the $(C_6H_5NH_3)Cl$ solution before the titration begins?
    b. What is the pH at the equivalence point?
    c. What is the pH at the half-equivalence point?
    d. Calculate the pH of the solution after adding 10.0, 20.0 and 30.0 mL of base.

Answers to the Practice Problem Set:

1. $[H_3O^+] = 1.5 \times 10^{-9}$ M; pH = 8.81
2. a. > 7 b. < 7 c. = 7
3. a. decreases b. increases c. no change
4. 9.25
5. 4.38
6. 4.7 g
7. pH = 9.11; lower pH than original solution
8. a. 3.59 b. 0.45
9. 4.92
10. answer (b)
11. 2 mol of base for every 1 mol of acid to some amount of water
12. a. 4.95 b. 5.05
13. a. 9.55 b. 9.50
14. a. pH = 5.62 b. $[Na^+] = 0.0323$ M, $[H_3O^+] = 6.5 \times 10^{-12}$ M, $[OH^-] = 0.0015$ M, $[C_6H_5O^-] = 0.0307$ M c. pH = 11.19
15. a. $[NH_3] = 0.0154$ M b. $[H_3O^+] = 1.9 \times 10^{-6}$ M, $[OH^-] = 5.3 \times 10^{-9}$ M, $[NH_4^+] = 0.00625$ M c. pH = 5.73
16. a. pH = 11.89 b. pH = 10.63 c. pH = 10.15 d. pH = 5.93 e. pH = 2.13 f. WB + SA curve (see titration lab) g. Alizarin or bromcresol purple (two possible examples)
17. a. pH = 11.13 b. pH = 5.28 c. pH = 9.25 d. methyl red (one possible answer) e. at 5.00 mL, pH = 9.85; at 15.00 mL, pH = 9.08; at 20.00 mL, pH = 8.65; at 22.00 mL, pH = 8.39; at 30.00 mL, pH = 2.04; graph = WB + SA curve (see titration lab)
18. a. pH = 2.81 b. pH = 8.72 c. pH = 4.62 d. at 10.00 mL, pH = 4.39; at 20.00 mL, pH = 5.07; at 30.00 mL, pH = 11.84

CH 223 Practice Problem Set #4

This is a ***practice problem set*** *and not the actual graded problem set that you will turn in for credit. Answers to each problem can be found at the end of this assignment.*

Covering: **Chapter Fifteen** (solubility), **Chapter Sixteen** *and* **Chapter Guide Four**
Important Tables and/or Constants: **Solubility Table** (*from the CH 221* Net Ionics *lab* or here: **https://mhchem.org/sol**), **"Solubility Product Constant (K_{sp}) Values at 25 °C"** *and* **"Complex Ion Formation Constant (K_f) Values at 25 °C"** *at the end of problem set #4*, "**Solubility Guide**" *(Handout)*, **Table of Thermodynamic Values** *(found at the end of CH 223 Problem Set #5 or here:* **http://mhchem.org/thermo**)

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1. Predict whether each of the following is insoluble or soluble in water.
   a. $(NH_4)_2CO_3$
   b. $ZnSO_4$
   c. NiS
   d. $BaSO_4$
2. For each of the following insoluble salts, (i) write a balanced equation showing the equilibrium occurring when the salt is added to water and (ii) write the K_{sp} expression.
   a. AgCN
   b. $NiCO_3$
   c. $AuBr_3$
3. When 1.55 g of solid thallium(I) bromide is added to 1.00 L of water, the salt dissolves to a small extent.
   $$TlBr(s) \rightleftharpoons Tl^{+}(aq) + Br^{-1}(aq)$$
   The thallium(I) and bromide ions in equilibrium with TlBr each have a concentration of 1.9×10^{-3} M. What is the value of K_{sp} for TlBr?
4. You add 0.979 g of $Pb(OH)_2$ to 1.00 L of pure water at 25 °C. The pH is 9.15. Estimate the value of K_{sp} for $Pb(OH)_2$.
5. Estimate the solubility of calcium fluoride, CaF_2, (a) in moles per liter and (b) in grams per liter of pure water.
   $$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^{-1}(aq) \quad K_{sp} = 5.3 \times 10^{-11}$$
6. The K_{sp} value for radium sulfate, $RaSO_4$, is 3.7×10^{-11}. If 25 mg of radium sulfate is placed in 1.00×10^2 mL of water, does all of it dissolve? If not, how much dissolves?
7. Use K_{sp} values to decide which compound in each of the following pairs is the more soluble.
   a. $PbCl_2$ ($K_{sp} = 1.7 \times 10^{-5}$) or $PbBr_2$ ($K_{sp} = 6.6 \times 10^{-6}$)
   b. HgS ($K_{sp} = 4.2 \times 10^{-11}$) or FeS ($K_{sp} = 8.0 \times 10^{-19}$)
   c. $Fe(OH)_2$ ($K_{sp} = 4.9 \times 10^{-17}$) or $Zn(OH)_2$ ($K_{sp} = 3.0 \times 10^{-17}$)
8. Compare the solubility, in milligrams per milliliter, of silver iodide, AgI, (a) in pure water and (b) in water that is 0.020 M in $AgNO_3$. (K_{sp} for AgI = 8.5×10^{-17})
9. You have a solution that has a lead(II) concentration of 0.0012 M.
   $$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^{-1}(aq)$$
   If enough soluble chloride-containing salt is added so that the Cl^{-1} concentration is 0.010 M, will $PbCl_2$ precipitate? (K_{sp} for $PbCl_2$ = 1.7×10^{-5})

11. Solid gold(I) chloride, AuCl, dissolves when excess cyanide ion, CN^{-1}, is added to give a water-soluble complex ion.

$$AuCl(s) + 2\ CN^{-1}(aq) \rightleftharpoons [Au(CN)_2]^{-1}(aq) + Cl^{-1}(aq)$$

Show that this equation is the sum of two other equations, one for dissolving AuCl to give its ions ($K_{sp} = 2.0 \times 10^{-13}$) and the other for the formation of the $[Au(CN)_2]^{-1}$ ion (using $K_{form} = 2.0 \times 10^{38}$) from Au^{+1} and CN^{-1}. Calculate K_{net} for the overall reaction.

12. Each pair of ions below is found together in aqueous solution. Using a table of solubility product constants, devise a way to separate these ions by precipitating one of them as an insoluble salt and leaving the other in solution.
    a. Ba^{2+} and Na^{+}
    b. Ni^{2+} and Pb^{2+}
13. A solution contains Ca^{2+} and Pb^{2+} ions, both at a concentration of 0.010 M. You wish to separate the two ions from each other as completely as possible by precipitating one but not the other using aqueous Na_2SO_4 as the precipitating agent.
    a. Which will precipitate first as sodium sulfate is added, $CaSO_4$ or $PbSO_4$?
    b. What will be the concentration of the first ion that precipitates (Ca^{2+} or Pb^{2+}) when the second, more soluble salt begins to precipitate?
14. Explain why the solubility of Ag_3PO_4 can be greater in water than is calculated from the K_{sp} value of the salt.
15. Which substance has the higher entropy in each of the following pairs?
    a. dry ice (solid CO_2) at -78 °C or $CO_2(g)$ at 0 °C
    b. liquid water at 25 °C or liquid water at 50 °C
    c. pure alumina, $Al_2O_3(s)$, or ruby (ruby is $Al_2O_3(s)$ in which some of the Al^{3+} ions in the crystalline lattice are replaced with Cr^{3+} ions.)
    d. one mole of $N_2(g)$ at 1 bar pressure or one mole of $N_2(g)$ at 10 bar pressure (both at 298 K)
16. By comparing the formulas for each pair of compounds, decide which is expected to have the higher entropy. Assume all are at the same temperature.
    a. $O_2(g)$ or $CH_3OH(g)$ (two substances with the same molar mass)
    b. HF(g), HCl(g), or HBr(g)
    c. $NH_4Cl(s)$ or $NH_4Cl(aq)$
    d. $HNO_3(g)$, $HNO_3(l)$, or $HNO_3(aq)$
17. Use $S°$ values to calculate the entropy change, $\Delta S°$, for each of the following processes and comment on the sign of the change.
    a. $LiOH(s) \rightarrow LiOH(aq)$ (*Note:* $S°(LiOH(aq)) = 91.6$ J/molK)
    b. $Na(g) \rightarrow Na(s)$
    c. $Br_2(l) \rightarrow Br_2(g)$
    d. $HCl(g) \rightarrow HCl(aq)$ (*Note:* $S°(HCl(aq)) = 56.5$ J/molK)
18. Calculate the standard molar entropy change of formation ($\Delta S_f°$) for each of the following compounds from the elements at 25 °C.
    a. HCl(g) b. $Ca(OH)_2(s)$
19. Calculate the standard molar entropy change for each of the following reactions at 25 °C. Comment on the sign of $\Delta S°$.
    a. $2\ Al(s) + 3\ Cl_2(g) \rightarrow 2\ AlCl_3(s)$
    b. $2\ CH_3OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(g)$

Answers to the Practice Problem Set:

1. (a) and (b): soluble, (c) and (d): insoluble
2. *Answers:*
   a. $AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$ $K_{sp} = [Ag^+][CN^-]$
   b. $NiCO_3(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = [Ni^{2+}][CO_3^{2-}]$
   c. $AuBr_3(s) \rightleftharpoons Au^{3+}(aq) + 3\ Br^-(aq)$ $K_{sp} = [Au^{3+}][Br^-]^3$
3. 3.6×10^{-6}
4. 1.4×10^{-15}
5. a. 2.4×10^{-4} b. 0.018
6. No; 0.20 mg dissolves
7. a. $PbCl_2$ b. HgS b. $Fe(OH)_2$
8. a. 2.2×10^{-6} b. 1.0×10^{-13}
9. $Q < K_{sp}$ so no precipitate
10. $Q > K_{sp}$ so precipitate forms
11. $K_{net} = 4.0 \times 10^{25}$
12. a. SO_4^{2-} will precipitate Ba^{2+} b. Cl^{-1} will precipitate Pb^{2+}
13. a. $PbSO_4$ b. 5.1×10^{-6} M
14. PO_4^{3-} acts as a base, increasing solubility upon formation of HPO_4^{2-}
15. a. $CO_2(g)$ b. 50° $H_2O(l)$ c. ruby d. $N_2(g)$ at 1 bar
16. a. $CH_3OH(g)$ b. HBr(g) c. $NH_4Cl(aq)$ d. $HNO_3(g)$
17. a. 48.8 J/K (entropy increase) b. -102.4 J/K (entropy decrease) c. 93.3 J/K (entropy increase) d. -130.4 J/K (entropy decrease) (*Instructor note:* your values of ΔS might be slightly different depending on the textbook used, etc., but they should be *close* to these values.)
18. a. 10.0 J/K b. -294.1 J/K (see note in answer #17, above)
19. a. -504.6 J/K (entropy increase) b. 313.6 J/K (entropy decrease) (see note in answer #17, above)

CH 223 Practice Problem Set #5

*This is a **practice problem set** and not the actual graded problem set that you will turn in for credit.*
Answers to each problem can be found at the end of this assignment.

Covering: **Chapter Sixteen, Chapter Seventeen** *and* **Chapter Guide Five**
Important Tables and/or Constants: **F = 96485 C/mol e$^-$, R = 8.3145 J mol^{-1} K^{-1}**, "**Redox Reactions**" *(Handout),* **Table of Redox Potentials** *at the end of problem set #5,* **Table of Thermodynamic values** *at the end of problem set #5 and here:* **http://mhchem.org/thermo**

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1. Classify each of the reactions according to their spontaneity. Are these reactions enthalpy and/or entropy driven?
   a. $Fe_2O_3(s) + 2\ Al(s) \rightarrow 2\ Fe(s) + Al_2O_3(s)$ $\Delta H° = -851.5$ kJ $\Delta S° = -375.2$ J/K
   b. $N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g)$ $\Delta H° = 66.2$ kJ; $\Delta S° = -121.6$ J/K
2. Heating some metal carbonates, among them calcium carbonate, leads to their decomposition.
   $$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$
   a. Calculate $\Delta H°$ and $\Delta S°$ for the reaction.
   b. Is the reaction spontaneous at 298 K?
   c. Is the reaction predicted to be spontaneous at higher temperatures?
3. Using values of $\Delta H°_f$ and $S°$, calculate $\Delta G°_{rxn}$ for the following reaction. Is the reaction product-favored? Is the reaction enthalpy or entropy driven?
   $$2\ Pb(s) + O_2(g) \rightarrow 2\ PbO(s, \text{yellow})$$
4. Using values of $\Delta G°_f$, calculate $\Delta G°_{rxn}$ for each of the following reactions. Which are product-favored?
   a. $2\ K(s) + Cl_2(g) \rightarrow 2\ KCl(s)$
   b. $2\ CuO(s) \rightarrow 2\ Cu(s) + O_2(g)$
   c. $4\ NH_3(g) + 7\ O_2(g) \rightarrow 4\ NO_2(g) + 6\ H_2O(g)$
5. For the reaction: $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$, $\Delta G°_{rxn} = +219.7$ kJ. Using this value and a table of thermodynamic data, calculate the value of $\Delta G°_f$ for $BaCO_3(s)$.
6. Estimate the temperature required to decompose HgS(s) into Hg(l) and S(g).
7. Calculate $\Delta G°$ and K_p at 25 °C for the reaction: $2\ HBr(g) + Cl_2(g) \rightarrow 2\ HCl(g) + Br_2(l)$ Is the reaction predicted to be product-favored under standard conditions? Comment on the sign of $\Delta G°$ and the magnitude of K_p.
8. Write balanced equations for the following half-reactions. Specify whether each is an oxidation or reduction.
   a. $Cr(s) \rightarrow Cr^{3+}(aq)$ (in acid)
   b. $AsH_3(g) \rightarrow As(s)$ (in acid)
   c. $VO_3^{-1}(aq) \rightarrow V^{2+}(aq)$ (in acid)
   d. $Ag(s) \rightarrow Ag_2O(s)$ (in base)

9. Balance the following redox equations. All occur in acid solution.
   a. $Ag(s) + NO_3^{-1}(aq) \rightarrow NO_2(g) + Ag^+(aq)$
   b. $MnO_4^{-1}(aq) + HSO_3^{-1}(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq)$
   c. $Zn(s) + NO_3^{-1}(aq) \rightarrow Zn^{2+}(aq) + N_2O(g)$
   d. $Cr(s) + NO_3^{-1}(aq) \rightarrow Cr^{3+}(aq) + NO(g)$
10. Balance the following redox equations. All occur in basic solution.
    a. $Al(s) + OH^{-1}(aq) \rightarrow Al(OH)_4^{-1}(aq) + H_2(g)$
    b. $CrO_4^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr(OH)_3(s) + SO_4^{2-}(aq)$
    c. $Zn(s) + Cu(OH)_2(s) \rightarrow [Zn(OH)_4]^{2-}(aq) + Cu(s)$
    d. $HS^{-1}(aq) + ClO_3^{-1}(aq) \rightarrow S(s) + Cl^{-1}(aq)$
11. A voltaic cell is constructed using the reaction of chromium metal and iron(II) ion.

    $$2\ Cr(s) + 3\ Fe^{2+}(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ Fe(s)$$

    Complete the following sentences: Electrons in the external circuit flow from the ___ electrode to the ___ electrode. Negative ions move in the salt bridge from the ___ half-cell to the ___ half-cell. The half-reaction at the anode is ___ and that at the cathode is ___.
12. The half-cells $Fe(s) \mid Fe^{2+}(aq) \parallel O_2(g, 1\ atm) \mid H_2O(l, pH = 1.0)$ are linked to create a voltaic cell.
    a. Write equations for the oxidation and reduction half-reactions and for the overall (cell) reaction.
    b. Which half-reaction occurs in the anode compartment and which occurs in the cathode compartment?
    c. Complete the following sentences: Electrons in the external circuit flow from the ___ electrode to the ___ electrode. Negative ions move in the salt bridge from the ___ half-cell to the ___ half-cell.
13. Balance each of the following *unbalanced* equations, then calculate the standard redox potential, $E°$, and decide whether each is product-favored as written. All reactions occur in acid solution.
    a. $Sn^{2+}(aq) + Ag(s) \rightarrow Sn(s) + Ag^{+1}(aq)$
    b. $Al(s) + Sn^{4+}(aq) \rightarrow Sn^{2+}(aq) + Al^{3+}(aq)$
    c. $ClO_3^{-1}(aq) + Ce^{3+}(aq) \rightarrow Cl^{-1}(aq) + Ce^{4+}(aq)$ *Look these cell potentials up online*
    d. $Cu(s) + NO_3^{-1}(aq) \rightarrow Cu^{2+}(aq) + NO(g)$

14. Consider the following half-reactions:

Half-Reaction	***E*° (V)**
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	+0.34
$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$	-0.14
$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$	-0.44
$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$	-1.66

   a. Based on $E°$ values, which metal is the most easily oxidized?
   b. Which metals on this list are capable of reducing $Fe^{2+}(aq)$ to Fe?
   c. Write a balanced chemical equation for the reaction of $Fe^{2+}(aq)$ with Sn(s). Is this reaction product-favored or reactant-favored?
   d. Write a balanced chemical equation for the reaction of $Zn^{2+}(aq)$ with Sn(s). Is this reaction product-favored or reactant-favored?

15. Calculate the voltage delivered by a voltaic cell using the following reaction if all dissolved species are 2.5×10^{-2} M. *Use the OpenStax text to find the cell potentials.*

$$Zn(s) + 2\ H_2O(l) + 2\ OH^{-1}(aq) \rightarrow [Zn(OH)_4]^{2-}(aq) + H_2(g)$$

16. Calculate $\Delta G°$ and the equilibrium constant for the following reactions.
   a. $2\ Fe^{3+}(aq) + 2\ I^{-1}(aq) \rightarrow 2\ Fe^{2+}(aq) + I_2(aq)$
   b. $I_2(aq) + 2\ Br^{-1}(aq) \rightarrow 2\ I^{-1}(aq) + Br_2(aq)$

17. A potential of +0.146 V is recorded (under standard conditions) for a voltaic cell constructed using the following half-reactions:

   Anode: $Ag(s) \rightarrow Ag^{+1}(aq) + e^-$
   Cathode: $Ag_2SO_4(s) + 2\ e^- \rightarrow 2\ Ag(s) + SO_4^{2-}(aq)$

   a. What is the standard reduction potential for the cathode reaction?
   b. Calculate the solubility product, K_{sp}, for Ag_2SO_4.

18. In the electrolysis of a solution containing $Ni^{2+}(aq)$, metallic Ni(s) deposits on the cathode. Using a current of 0.150 A for 12.2 min, what mass of nickel will form?

19. Electrolysis of a solution of $CuSO_4(aq)$ to give copper metal is carried out using a current of 0.66 A. How long should electrolysis continue to produce 0.50 g of copper?

20. Electrolysis of molten NaCl is done in cells operating at 7.0 V and 4.0×10^4 A. What mass of Na(s) and $Cl_2(g)$ can be produced in one day in such a cell? What is the energy consumption in kilowatt-hours? (1 kWh = 3.6×10^6 J and 1 J = 1 C • V)

Answers to the Practice Problem Set: ***Please note*** *that all thermodynamic and electrochemical answers will vary slightly depending on the source of values used to solve the problems. The answers should be close, however.*

1. a. enthalpy driven, spontaneous at low temperatures b. non-spontaneous at all temperatures
2. a. $\Delta H^\circ = 191.59$ kJ, $\Delta S^\circ = 141.9$ J/K b. no c. yes
3. $\Delta H^\circ = -434.64$ kJ, $\Delta S^\circ = -197.4$ J/K, $\Delta G^\circ = -375.77$ kJ; product favored, enthalpy driven
4. a. $\Delta G^\circ = -817.0$ kJ; product favored b. $\Delta G^\circ = 259.4$ kJ; reactant favored c. $\Delta G^\circ = -1101.3$ kJ; product favored
5. $\Delta G_f^\circ[\mathrm{BaCO_3(s)}] = -1134.4$ kJ/mol
6. 2089 K or greater
7. $\Delta G^\circ = -83.74$ kJ; $K_\mathrm{p} = 4.8 \times 10^{14}$ Negative ΔG and large K_p indicate product-favored reaction
8. *Answers:*
    a. $\mathrm{Cr(s) \rightarrow Cr^{3+}(aq) + 3\ e^-}$ oxidation
    b. $\mathrm{AsH_3(g) \rightarrow As(s) + 3\ H^+(aq) + 3\ e^-}$ oxidation
    c. $\mathrm{VO_3^-(aq) + 6\ H^+(aq) + 3\ e^- \rightarrow V^{2+}(aq) + 3\ H_2O(\ell)}$ reduction
    d. $\mathrm{2\ Ag(s) + 2\ OH^-(aq) \rightarrow Ag_2O(s) + H_2O(\ell) + 2\ e^-}$ oxidation
9. *Answers:*
    a. $\mathrm{Ag(s) + NO_3^-(aq) + 2\ H^+(aq) \rightarrow Ag^+(aq) + NO_2(g) + H_2O(\ell)}$
    b. $\mathrm{2\ MnO_4^-(aq) + H^+(aq) + 5\ HSO_3^-(aq) \rightarrow 2\ Mn^{2+}(aq) + 3\ H_2O(\ell) + 5\ SO_4^{2-}(aq)}$
    c. $\mathrm{4\ Zn(s) + 2\ NO_3^-(aq) + 10\ H^+(aq) \rightarrow 5\ H_2O(\ell) + 4\ Zn^{2+}(aq) + N_2O(g)}$
    d. $\mathrm{Cr(s) + NO_3^-(aq) + 4\ H^+(aq) \rightarrow Cr^{3+}(aq) + NO(g) + 2\ H_2O(\ell)}$
10. *Answers:*
    a. $\mathrm{2\ Al(s) + 6\ H_2O(\ell) + 2\ OH^-(aq) \rightarrow 2\ Al(OH)_4^-(aq) + 3\ H_2(g)}$
    b. $\mathrm{2\ CrO_4^-(aq) + 5\ H_2O(\ell) + 3\ SO_3^{2-}(aq) \rightarrow 2\ Cr(OH)_3(s) + 4\ OH^-(aq) + 3\ SO_4^{2-}(aq)}$
    c. $\mathrm{Zn(s) + 2\ OH^-(aq) + Cu(OH)_2(s) \rightarrow Zn(OH)_4^{2-}(aq) + Cu(s)}$
    d. $\mathrm{3\ HS^-(aq) + ClO_3^-(aq) \rightarrow 3\ S(s) + Cl^-(aq) + 3\ OH^-(aq)}$
11. Electrons in the external circuit flow from the Cr electrode to the Fe electrode. Negative ions move in the salt bridge from the $\mathrm{Fe/Fe^{2+}}$ half-cell to the $\mathrm{Cr/Cr^{3+}}$ half-cell. The half-reaction at the anode is $\mathrm{Cr(s) \rightarrow Cr^{3+}(aq) + 3\ e^-}$ and that at the cathode is $\mathrm{Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)}$.
12. *Answers:*
    a. Oxidation: $\mathrm{Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-}$
    Reduction: $\mathrm{O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(\ell)}$
    Overall: $\mathrm{2\ Fe(s) + O_2(g) + 4\ H^+(aq) \rightarrow 2\ H_2O(\ell) + 2\ Fe^{2+}(aq)}$

    b. Oxidation occurs in the anode compartment and reduction occurs in the cathode compartment.

    c. Electrons in the external circuit flow from the Fe electrode to the positive (site of O_2 reduction) electrode. Negative ions move in the salt bridge from the $\mathrm{O_2/H_2O}$ half-cell to the $\mathrm{Fe/Fe^{2+}}$ half-cell.

13. Answers:

a. $Sn^{2+}(aq) + 2\ Ag(s) \rightarrow Sn(s) + 2\ Ag^{+}(aq)$
   $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (-0.14\ V) - (+0.799\ V) = -0.94\ V$ not product-favored
b. $2\ Al(s) + 3\ Sn^{4+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Sn^{2+}(aq)$
   $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (+0.15\ V) - (-1.66\ V) = +1.81\ V$ product-favored
c. $ClO_3^{-}(aq) + 6\ H^{+}(aq) + 6\ Ce^{3+}(aq) \rightarrow Cl^{-}(aq) + 3\ H_2O(\ell) + 6\ Ce^{4+}(aq)$
   $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (+0.62\ V) - (+1.61\ V) = -0.99\ V$ not product-favored
d. $3\ Cu(s) + 2\ NO_3^{-}(aq) + 8\ H^{+}(aq) \rightarrow 2\ NO(g) + 3\ Cu^{2+}(aq) + 4\ H_2O(\ell)$
   $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (+0.96\ V) - (+0.337\ V) = +0.62\ V$ product-favored

14. Answers:

a. Al(s)
b. Zn(s) and Al(s)
c. $Fe^{2+}(aq) + Sn(s) \rightarrow Fe(s) + Sn^{2+}(aq)$
   $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (-0.44\ V) - (-0.14\ V) = -0.30\ V$ reactant-favored
d. $Zn^{2+}(aq) + Sn(s) \rightarrow Zn(s) + Sn^{2+}(aq)$
   $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (-0.76\ V) - (-0.14\ V) = -0.62\ V$ reactant-favored

15. 0.32 V
16. a. $\Delta G^{o} = -45.5$ kJ, $K = 9 \times 10^{7}$ b. $\Delta G^{o} = 110$ kJ, $K = 4 \times 10^{-19}$
17. a. 0.653 V b. $K_{sp} = 1 \times 10^{-5}$
18. 0.0334 g
19. 2300 s (38 min)
20. 8.2×10^{5} g Na, 1.3×10^{6} g Cl_2, 6700 kwh

CH 223 Practice Problem Set #6

*This is a **practice problem set** and not the actual graded problem set that you will turn in for credit. Answers to each problem can be found at the end of this assignment.*

Covering: **Chapters Eighteen** *and* **Chapter Nineteen** *and* **Chapter Guide Six**
Important Tables and/or Constants: "**Coordination Compounds**" *(Handout)*

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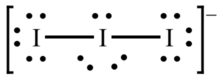
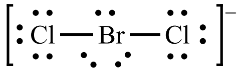
1. Write balanced chemical equations for the reaction of hydrogen gas with oxygen, chlorine, and nitrogen.
2. Write a balanced chemical equation for the preparation of H_2 (and CO) by the reaction of CH_4 and water. Using a table of thermodynamic data, calculate $\Delta H°$, $\Delta G°$, and $\Delta S°$ for this reaction.
3. Complete and balance the equations for the following reactions.
   a. $Na(s) + Br_2(l) \rightarrow$
   b. $Mg(s) + O_2(g) \rightarrow$
   c. $Al(s) + F_2(g) \rightarrow$
   d. $C(s) + O_2(g) \rightarrow$ (assume an excess of oxygen has been added)
4. Calcium oxide, CaO, is used to remove SO_2 from power plant exhaust. These two compounds react to give solid $CaSO_3$. What mass of SO_2 can be removed using 1.2×10^3 kg of CaO?
5. Aluminum dissolves readily in hot aqueous NaOH to give the aluminate ion, $Al(OH)_4^{-1}$, and H_2. Write a balanced equation for this reaction. If you begin with 13.2 g of Al, what volume (in milliliters) of H_2 gas is produced when the gas is measured at 735 mm Hg and 22.5 °C?
6. Use a table of thermodynamic data to calculate the enthalpy and free energy change for the reaction: $\mathbf{2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)}$ Is this reaction exothermic or endothermic? Is the reaction product- or reactant-favored?
7. Write the balanced equation for the reaction of hydrazine in acid solution ($N_2H_5^{+1}$) with $IO_3^{-1}(aq)$ to give N_2 and I_2. Calculate $E°$ for this reaction using a table of reduction potentials (look online for these values.)
8. If an electrolytic3cell for producing F_2 operates at 5.00×10^3 amps (at 10.0 V), what mass of F_2 can be produced per 24-hour day? Assume the conversion of F^{-1} to F_2 is 100%.
9. When BCl_3 gas is passed through an electric discharge, small amounts of the reactive molecule B_2Cl_4 are produced. (The molecule has a B-B covalent bond.)
   a. Draw a Lewis electron dot structure for B_2Cl_4.
   b. Describe the hybridization of the B atoms in the molecule and the geometry around each B atom.
10. How would you extinguish a sodium fire in the laboratory? What is the worst thing you could do?
11. You are given a stoppered flask that contains either hydrogen, nitrogen, or oxygen. Suggest an experiment to identify the gas.
12. Halogens form polyhalide ions. Sketch Lewis electron dot structures and describe the molecular geometry for the following ions:
    a. I_3^{-1}
    b. $BrCl_2^{-1}$
    c. ClF_2^{+1}

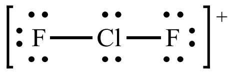
13. Give the electron configuration for each of the following ions, and tell whether each is paramagnetic or diamagnetic.
    a. Cr^{3+}
    b. V^{2+}
    c. Ni^{2+}
    d. Cu^{+}
14. The following equations represent various ways of obtaining transition metals from their compounds. Balance each equation.
    a. $Cr_2O_3(s) + Al(s) \rightarrow Al_2O_3(s) + Cr(s)$
    b. $TiCl_4(l) + Mg(s) \rightarrow Ti(s) + MgCl_2(s)$
    c. $[Ag(CN)_2]^{-1}(aq) + Zn(s) \rightarrow Ag(s) + [Zn(CN)_4]^{2-}(aq)$
    d. $Mn_3O_4(s) + Al(s) \rightarrow Mn(s) + Al_2O_3(s)$
15. Which of the following ligands is expected to be monodentate and which might be polydentate?
    a. CH_3NH_2 b. CH_3CN c. N_3^{-1} d. en e. Br^{-1} f. phen
16. Give the oxidation number of the metal ion in each of the following compounds.
    a. $[Mn(NH_3)_6]SO_4$ b. $K_3[Co(CN)_6]$ c. $[Co(NH_3)_4Cl_2]Cl$ d. $Cr(en)_2Cl_2$
17. Write formulas for the following ions or compounds.
    a. dichlorobis(ethylenediamine)nickel(II)
    b. potassium tetrachloroplatinate(II)
    c. potassium dicyanocuprate(I)
    d. tetraamminediaquairon(II)
18. Name the following ions or compounds.
    a. $[Ni(C_2O_4)_2(H_2O)_2]^{2-}$
    b. $[Co(en)_2Br_2]^{+1}$
    c. $[Co(en)_2(NH_3)Cl]^{2+}$
    d. $Pt(NH_3)_2(C_2O_4)$
19. Give the name or formula for each ion or compound, as appropriate.
    a. pentaaquahydroxoiron(III) ion
    b. $K_2[Ni(CN)_4]$
    c. $K[Cr(C_2O_4)_2(H_2O)_2]$
    d. ammonium tetrachloroplatinate(II)
20. Draw all possible geometric isomers of the following.
    a. $Fe(NH_3)_4Cl_2$
    b. $Pt(NH_3)_2(SCN)(Br)$ (SCN^{-1} is bonded to Pt^{2+} through S)
    c. $Co(NH_3)_2(NO_2)_3$ (NO_2^{-1} is bonded to Co^{3+} through N)
    d. $[Co(en)Cl_2]^{-1}$
21. In water, the titanium(III) ion, $[Ti(H_2O)_6]^{3+}$, has a broad absorption band at about 500 nm. What color light is absorbed by the ion?
22. A transition metal complex absorbs 425-nm light. What is its color?
    a. red b. green c. yellow d. blue
23. Give the formula of the complex formed from one Co^{3+} ion, two ethylenediamine molecules, one water molecule, and one chloride ion. Is the complex neutral or charged? If charged, give the net charge on the ion.

Answers to the Practice Problem Set:

1. *Answers:*
   $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$
   $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$
   $3\ H_2(g) + N_2(g) \rightarrow 2\ NH_3(g)$
2. $CH_4(g) + H_2O(g) \rightarrow 3\ H_2(g) + CO(g)$; $\Delta H^\circ = 205.9$ kJ, $\Delta S^\circ = 214.7$ J/K, $\Delta G^\circ = 141.9$ kJ (*Note:* Answers will vary depending on table used)
3. *Answers:*
   a. $2\ Na(s) + Br_2(\ell) \rightarrow 2\ NaBr(s)$
   b. $2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$
   c. $2\ Al(s) + 3\ F_2(g) \rightarrow 2\ AlF_3(g)$
   d. $C(s) + O_2(g) \rightarrow CO_2(g)$
4. 1.4×10^6 g
5. $2\ Al(s) + 2\ NaOH(aq) + 6\ H_2O(\ell) \rightarrow 2\ Na^+(aq) + 2\ Al(OH)_4^-(aq) + 3\ H_2(g)$; 1.84×10^4 mL
6. $\Delta H^\circ = -114.1$ kJ, $\Delta G^\circ = -72.6$ J/K; exothermic and product-favored
7. $5\ N_2H_5^+(aq) + 4\ IO_3^-(aq) \rightarrow 5\ N_2(g) + H^+(aq) + 2\ I_2(aq) + 12\ H_2O(\ell)$; $E^\circ = (1.195 - (-0.23)) = 1.43$ V (*Note:* Answers will vary depending on table used)
8. 8.51×10^4 g
9. a. B-B single bond, each B has two Cl atoms connected via sigma bond b. *sp*^{2}, trigonal planar
10. Use inert dry chemical fire extinguisher; Na reacts with water!
11. Insert glowing splint: H will ignite, O will burst into flame, N will extinguish flint
12. *Answers:*

a.  linear

b.  linear

c.  bent

13. a. [Ar]3d^3, paramagnetic b. [Ar]3d^3, paramagnetic c. [Ar]3d^8, paramagnetic d. [Ar]3d^{10}, diamagnetic
14. *Answers:*
   a. $Cr_2O_3(s) + 2\ Al(s) \rightarrow Al_2O_3(s) + 2\ Cr(s)$
   b. $TiCl_4(\ell) + 2\ Mg(s) \rightarrow Ti(s) + 2\ MgCl_2(s)$
   c. $2\ [Ag(CN)_2]^-(aq) + Zn(s) \rightarrow 2\ Ag(s) + [Zn(CN)_4]^{2-}(aq)$
   d. $3\ Mn_3O_4(s) + 8\ Al(s) \rightarrow 9\ Mn(s) + 4\ Al_2O_3(s)$
15. *monodentate:* a, b, c, e *polydentate:* d, f
16. a. Mn^{2+} b. Co^{3+} c. Co^{3+} d. Cr^{2+}
17. a. $[NiCl_2(en)_2]$ b. $K_2[PtCl_4]$ c. $K[Cu(CN)_2]$ d. $[Fe(NH_3)_4(H_2O)_2]^{2+}$

18. Answers:

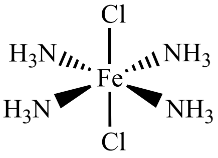
a. diaquabis(oxalato)nickelate(II) ion
b. dibromobis(ethylenediamine)cobalt(II) ion
c. amminechlorobis(ethylenediamine)cobalt(III) ion
d. diammineoxalatoplatinum(II)

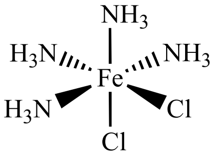
19. Answers:

(a) $[Fe(H_2O)_5OH]^{2+}$
(b) potassium tetracyanonickelate(II)
(c) potassium diaquabis(oxalato)chromate(III)
(d) $(NH_4)_2[PtCl_4]$

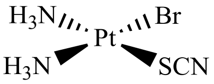
20. Answers:

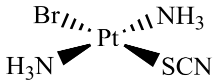
a.



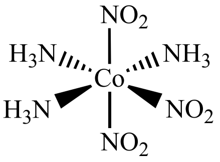


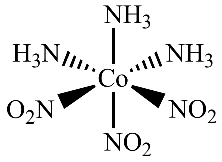
b.



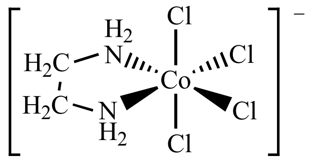


c.





d.



21. yellow
22. yellow
23. $[Co(en)_2(H_2O)Cl]^+$, aquachlorobis(ethylenediamine)cobalt(III) ion. The complex has a +1 charge

Concentrations, pH, Acids, Bases and Redox - *Answers at end*

1. If 10.0 mL of 0.100 *M* HCl is titrated with 0.200 *M* NaOH, what volume of sodium hydroxide solution is required to neutralize the acid?

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

2. If 20.0 mL of 0.500 *M* KOH is titrated with 0.250 *M* HNO_3, what volume of nitric acid is required to neutralize the base?

$$HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$$

3. If 25.0 mL of 0.100 *M* HCl is titrated with 0.150 *M* $Ba(OH)_2$, what volume of barium hydroxide is required to neutralize the acid?

$$2\ HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2\ H_2O(l)$$

4. If 25.0 mL of 0.100 *M* $Ca(OH)_2$ is titrated with 0.200 *M* HNO_3, what volume of nitric acid is required to neutralize the base?

$$2\ HNO_3(aq) + Ca(OH)_2(aq) \rightarrow 2\ Ca(NO_3)_2(aq) + 2\ H_2O(l)$$

5. If 20.0 mL of 0.200 *M* H_2SO_4 is titrated with 0.100 *M* NaOH, what volume of sodium hydroxide is required to neutralize the acid?

$$H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$$

6. If 30.0 mL of 0.100 *M* $Ca(OH)_2$ is titrated with 0.150 *M* $HC_2H_3O_2$, what volume of acetic acid is required to neutralize the base?

$$2\ HC_2H_3O_2(aq) + Ca(OH)_2(aq) \rightarrow Ca(C_2H_3O_2)_2(aq) + 2\ H_2O(l)$$

7. If a 50.0 mL sample of ammonium hydroxide is titrated with 25.0 mL of 0.200 *M* nitric acid to a methyl red endpoint, what is the molarity of the base?

$$NH_4OH(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$$

8. If a 50.0 mL sample of ammonium hydroxide is titrated with 25.0 mL of 0.200 *M* sulfuric acid to a methyl red endpoint, what is the molarity of the base?

$$2\ NH_4OH(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq) + 2\ H_2O(l)$$

9. If a 25.0 mL sample of sulfuric acid is titrated with 50.0 mL of 0.200 *M* potassium hydroxide to a phenolphthalein endpoint, what is the molarity of the acid?

$$H_2SO_4(aq) + 2\ KOH(aq) \rightarrow K_2SO_4(aq) + 2\ H_2O(l)$$

10. What is the molarity of a hydrochloric acid solution if 20.00 mL of HCl is required to neutralize 0.424 g of sodium carbonate (105.99 g/mol)?

$$2\ HCl(aq) + Na_2CO_3(aq) \rightarrow 2\ NaCl(aq) + H_2O(l) + CO_2(g)$$

11. What is the molarity of a nitric acid solution if 25.00 mL of HNO_3 is required to neutralize 0.424 g of sodium carbonate (105.99 g/mol)?

$$2\ HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2\ NaNO_3(aq) + H_2O(l) + CO_2(g)$$

12. What is the molarity of a sulfuric acid solution if 30.00 mL of H_2SO_4 is required to neutralize 0.840 g of sodium hydrogen carbonate (84.01 g/mol)?

$$H_2SO_4(aq) + 2\ NaHCO_3(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l) + 2\ CO_2(g)$$

13. What is the molarity of a hydrochloric acid solution if 25.00 mL of HCl is required to neutralize 0.500 g of calcium carbonate (100.09 g/mol)?

$$2\ HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

14. What is the molarity of a sodium hydroxide solution if 40.00 mL of NaOH is required to neutralize 0.900 g of oxalic acid, $H_2C_2O_4$, (90.04 g/mol)?

$$H_2C_2O_4(aq) + 2\ NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2\ H_2O(l)$$

15. What is the molarity of a sodium hydroxide solution if 35.00 mL of NaOH is required to neutralize 1.555 g of KHP, that is $KHC_8H_4O_4$ (204.23 g/mol)?

$$KHC_8H_4O_4(aq) + NaOH(aq) \rightarrow KNaC_8H_4O_4(aq) + H_2O(l)$$

16. If a 0.200 g sample of sodium hydroxide (40.00 g/mol) is completely neutralized with 0.100 *M* H_2SO_4, what volume of sulfuric acid is required?

$$H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$$

17. If 0.900 g of oxalic acid, $H_2C_2O_4$, (90.04 g/mol) is completely neutralized with 0.300 *M* NaOH, what volume of sodium hydroxide is required?

$$H_2C_2O_4(aq) + 2\ NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2\ H_2O(l)$$

18. If 1.020 g of $KHC_8H_4O_4$ (204.23 g/mol) is completely neutralized with 0.200 *M* $Ba(OH)_2$, what volume of barium hydroxide is required?

$$2\ KHC_8H_4O_4(aq) + Ba(OH)_2(aq) \rightarrow BaK_2(C_8H_4O_4)_2(aq) + 2\ H_2O(l)$$

19. Glycine is an amino acid that can be abbreviated HGly. If 27.50 mL of 0.120 *M* NaOH neutralizes 0.248 g of HGly, what is the molar mass of the amino acid?

$$HGly(aq) + NaOH(aq) \rightarrow NaGly(aq) + H_2O(l)$$

20. Proline is an amino acid that can be abbreviated HPro. If 33.55 mL of 0.150 *M* NaOH neutralizes 0.579 g of HPro, what is the molar mass of the amino acid?

$$\text{HPro(aq)} + \text{NaOH(aq)} \rightarrow \text{NaPro(aq)} + H_2O(l)$$

21. Lactic acid is found in sour milk and can be abbreviated HLac. If 47.50 mL of 0.275 *M* NaOH neutralizes 1.180 g of HLac, what is the molar mass of the acid?

$$\text{HLac(aq)} + \text{NaOH(aq)} \rightarrow \text{NaLac(aq)} + H_2O(l)$$

22. What is the pH of an aqueous solution if the $[H^+] = 5.5\text{x}10^{-3}$ *M*?

23. What is the pH of an aqueous solution if the $[H^+] = 4.2\text{x}10^{-5}$ *M*?

24. What is the pH of an aqueous solution if the $[H^+] = 7/5\text{x}10^{-8}$ *M*?

25. What is the $[H^+]$ in an acid rain sample that has a pH = 3.22?

26. What is the $[H^+]$ in a blood sample that has a pH = 7.30?

27. What is the $[H^+]$ in a bleach sample that has a pH = 9.55?

28. What is the $[OH^-]$ in a seawater sample that has a pH = 8.65?

29. What is the $[OH^-]$ in an ammonia solution that has a pH = 10.20?

30. What is the $[OH^-]$ in an oven-cleaning solution that has a pH = 12.35?

31. What substance is oxidized in the following redox reaction?

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

32. What substance is reduced in the following redox reaction?

$$Co(s) + 2\,HCl(aq) \rightarrow CoCl_2(aq) + H_2(g)$$

33. What substance is oxidized in the following redox reaction?

$$F_2(g) + 2\,Br^-(aq) \rightarrow 2\,F^-(aq) + Br_2(l)$$

34. What substance is oxidized in the following redox reaction?

$$HgCl_2(aq) + Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + Hg_2Cl_2(s) + Cl^-(aq)$$

35. What substance is reduced in the following redox reaction?

$$H^+(aq) + Fe(s) + NO_3^-(aq) \rightarrow Fe^{3+}(aq) + NO(aq) + H_2O(l)$$

Acids, Bases, pH, and Redox - *Answers*

1. If 10.0 mL of 0.100 *M* HCl is titrated with 0.200 *M* NaOH, what volume of sodium hydroxide solution is required to neutralize the acid?

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

$M_1V_1 = M_2V_2$ (0.100M) (0.010L) = (0.200M)(V_2) V_2 = 0.005 L = **5 mL**

2. If 20.0 mL of 0.500 *M* KOH is titrated with 0.250 *M* HNO_3, what volume of nitric acid is required to neutralize the base?

$$HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$$

$M_1V_1 = M_2V_2$ (0.500M) (0.020L) = (0.250M)(V_2) V_2 = 0.040 L = **40 mL**

3. If 25.0 mL of 0.100 *M* HCl is titrated with 0.150 *M* $Ba(OH)_2$, what volume of barium hydroxide is required to neutralize the acid?

$$2\ HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2\ H_2O(l)$$

$M_1V_1 = M_2V_2$ (0.100M) (0.025L) = (0.150M)(V_2) V_2 = 0.0166 L = 16.6 mL OH^-

But there are 2 OH's per $Ba(OH)_2$ so it takes half this volume = **8.33 mL of $Ba(OH)_2$**

4. If 25.0 mL of 0.100 *M* $Ca(OH)_2$ is titrated with 0.200 *M* HNO_3, what volume of nitric acid is required to neutralize the base?

$$2\ HNO_3(aq) + Ca(OH)_2(aq) \rightarrow 2\ Ca(NO_3)_2(aq) + 2\ H_2O(l)$$

$M_1V_1 = M_2V_2$ (0.100M) (0.025L) = (0.200M)(V_2) V_2 = 0.0125 L = 12.5 mL H+

But it takes 2 HNO_3's per $Ca(OH)_2$ so it takes twice this volume = **25 mL of HNO_3**

5. If 20.0 mL of 0.200 *M* H_2SO_4 is titrated with 0.100 *M* NaOH, what volume of sodium hydroxide is required to neutralize the acid?

$$H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$$

0.200 M H_2SO_4 = 0.400 M H^+

$M_1V_1 = M_2V_2$ (0.40M) (0.020L) = (0.100M)(V_2) V_2 = 0.080 L = **80 mL NaOH**

6. If 30.0 mL of 0.100 *M* $Ca(OH)_2$ is titrated with 0.150 *M* $HC_2H_3O_2$, what volume of acetic acid is required to neutralize the base?

$$2\ HC_2H_3O_2(aq) + Ca(OH)_2(aq) \rightarrow Ca(C_2H_3O_2)_2(aq) + 2\ H_2O(l)$$

0.100 M $Ca(OH)_2$ = 0.200 M OH^-

$M_1V_1 = M_2V_2$ (0.200M) (0.030L) = (0.150M)(V_2) V_2 = 0.040 L = **40 mL NaOH**

7. If a 50.0 mL sample of ammonium hydroxide is titrated with 25.0 mL of 0.200 *M* nitric acid to a methyl red endpoint, what is the molarity of the base?

$$NH_4OH(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$$

$M_1V_1 = M_2V_2$ (0.200M) (0.025L) = (M_2)(0.050L) M_2 = 0.100 M NH_4OH

8. If a 50.0 mL sample of ammonium hydroxide is titrated with 25.0 mL of 0.200 *M* sulfuric acid to a methyl red endpoint, what is the molarity of the base?

$$2\ NH_4OH(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq) + 2\ H_2O(l)$$

0.200 M H_2SO_4 = 0.400 M H^+

$M_1V_1 = M_2V_2$ (0.400M) (0.025L) = (M_2)(0.050L) M_2 = **0.200 M NH_4OH**

9. If a 25.0 mL sample of sulfuric acid is titrated with 50.0 mL of 0.200 *M* potassium hydroxide to a phenolphthalein endpoint, what is the molarity of the acid?

$$H_2SO_4(aq) + 2\ KOH(aq) \rightarrow K_2SO_4(aq) + 2\ H_2O(l)$$

$M_1V_1 = M_2V_2$ (0.200M) (0.050L) = (M_2)(0.025L) M_2 = 0.400 M H^+

But, there are 2 H's per H_2SO_4 so [H_2SO_4] = **0.200M**

10. What is the molarity of a hydrochloric acid solution if 20.00 mL of HCl is required to neutralize 0.424 g of sodium carbonate (105.99 g/mol)?

$$2\ HCl(aq) + Na_2CO_3(aq) \rightarrow 2\ NaCl(aq) + H_2O(l) + CO_2(g)$$

0.424 g/105.99 g/mol = 0.0040 mol Na_2CO_3

Each Na_2CO_3 requires 2 HCl so we need 0.0080 mol HCl

MV = moles (M)(0.020L) = 0.0080 mole HCl M = **0.40 M HCl**

11. What is the molarity of a nitric acid solution if 25.00 mL of HNO_3 is required to neutralize 0.424 g of sodium carbonate (105.99 g/mol)?

$$2\ HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2\ NaNO_3(aq) + H_2O(l) + CO_2(g)$$

0.424 g/105.99 g/mol = 0.0040 mol Na_2CO_3

Each Na_2CO_3 requires 2 HNO_3 so we need 0.0080 mol HNO_3

MV = moles (M)(0.025L) = 0.0080 mole HNO_3 M = **0.32 M HNO_3**

12. What is the molarity of a sulfuric acid solution if 30.00 mL of H_2SO_4 is required to neutralize 0.840 g of sodium hydrogen carbonate (84.01 g/mol)?

$$H_2SO_4(aq) + 2\ NaHCO_3(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l) + 2\ CO_2(g)$$

0.840 g / 84.01 g/mol = 0.010 mol $NaHCO_3$

It takes 2 NaHCO3 per H_2SO_4 so you need 0.005 mol H_2SO_4

MV = moles M(0.030L) = 0.005 moles M = **0.167 M H_2SO_4**

13. What is the molarity of a hydrochloric acid solution if 25.00 mL of HCl is required to neutralize 0.500 g of calcium carbonate (100.09 g/mol)?

$$2\ HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

0.500 g/100.09 g/mol = 0.005 mol $CaCO_3$

Each mole of CaCO3 requires 2 mol HCl so you need 0.005 x 2 = 0.010 mol HCl

MV = moles M(0.025L) = 0.010 mol M = **0.40 M HCl**

14. What is the molarity of a sodium hydroxide solution if 40.00 mL of NaOH is required to neutralize 0.900 g of oxalic acid, $H_2C_2O_4$, (90.04 g/mol)?

$$H_2C_2O_4(aq) + 2\ NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2\ H_2O(l)$$

0.900 g / 90.04 g/mol = 0.010 mol Oxalic acid

It takes 2 mole NaOH for every mole of Oxalic acid

so you need 2 x 0.010 mol = 0.02 mol NaOH

MV = moles M(0.040L) = 0.020 mole NaOH **M = 0.50 M NaOH**

15. What is the molarity of a sodium hydroxide solution if 35.00 mL of NaOH is required to neutralize 1.555 g of KHP, that is $KHC_8H_4O_4$ (204.23 g/mol)?

$$KHC_8H_4O_4(aq) + NaOH(aq) \rightarrow KNaC_8H_4O_4(aq) + H_2O(l)$$

1.555g / 204.23 g/mol = 0.00761 mol KHP

1 mole KHP needs 1 mole of NaOH so, 0.00761 mole KHP = 0.00761 mole NaOH 0.00761

mole NaOH / 0.0351 L = **0.2175 M NaOH**

16. If a 0.200 g sample of sodium hydroxide (40.00 g/mol) is completely neutralized with 0.100 *M* H_2SO_4, what volume of sulfuric acid is required?

$$H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$$

0.200 g NaOH / 40 g/mol = 0.005 mol NaOH

1 mole of H_2SO_4 needs 2 mole NaOH so 0.005 mole NaOH needs 0.0025 mole H_2SO_4

MV = moles (0.100 M H_2SO_4) (V) = 0.0025 mole V = 0.0250 L = **25 mL**

17. If 0.900 g of oxalic acid, $H_2C_2O_4$, (90.04 g/mol) is completely neutralized with 0.300 *M* NaOH, what volume of sodium hydroxide is required? $H_2C_2O_4(aq)$

$$+ 2\ NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2\ H_2O(l)$$

0.900 g / 90.04 g/mol = 0.010 mol Oxalic acid

It takes 2 mole NaOH for every mole of Oxalic acid

so you need 2 x 0.010 mol = 0.02 mol NaOH

MV = moles (0.300M) (V) = 0.020 mole NaOH V = 0.0666 L = **66.6 mL**

18. If 1.020 g of $KHC_8H_4O_4$ (204.23 g/mol) is completely neutralized with 0.200 *M* $Ba(OH)_2$, what volume of barium hydroxide is required?

$$2\ KHC_8H_4O_4(aq) + Ba(OH)_2(aq) \rightarrow BaK_2(C_8H_4O_4)_2(aq) + 2\ H_2O(l)$$

1.020g / 204.23 g/mol = 0.0050 mol KHP

2 mole KHP needs 1 mole of $Ba(OH)_2$ so, 0.0050 mole KHP needs 0.0025 mole $Ba(OH)_2$

MV = moles (0.200 M) (V) = 0.0025 mole $Ba(OH)_2$ V = 0.01250 L = **12.5 mL**

19. Glycine is an amino acid that can be abbreviated HGly. If 27.50 mL of 0.120 *M* NaOH neutralizes 0.248 g of HGly, what is the molar mass of the amino acid?

HGly(aq) + NaOH(aq) → NaGly(aq) +

H_2O(l)

MV = moles (0.120 M) (0.02750L) = 0.033 mole NaOH = 0.0033 mole HGly

0.248 g / 0.0033 mole HGly = 75.12 g/mol HGly

20. Proline is an amino acid that can be abbreviated HPro. If 33.55 mL of 0.150 *M* NaOH neutralizes 0.579 g of HPro, what is the molar mass of the amino acid?

HPro(aq) + NaOH(aq) → NaPro(aq) + H_2O(l)

MV = moles (0.150 M) (0.03355L) = 0.005033 mole NaOH = 0.005033 mole HPro

0.579 g / 0.050033 mole HPro = **115.05 g/mol HPro**

21. Lactic acid is found in sour milk and can be abbreviated HLac. If 47.50 mL of 0.275
M NaOH neutralizes 1.180 g of HLac, what is the molar mass of the acid?

HLac(aq) + NaOH(aq) → NaLac(aq) + H_2O(l)

MV = moles (0.275 M) (0.0475L) = 0.01306 mole NaOH = 0.01306 mole HLac

1.180 g / 0.01306 mole HLac = **90.33 g/mol HLac**

22. What is the pH of an aqueous solution if the [H^+] = 5.5×10^{-3}

M? pH = - log [H^+] pH = - log [5.5×10^{-3}] = **2.26**

23. What is the pH of an aqueous solution if the [H^+] = 4.2×10^{-5}

M? pH = - log [H^+] pH = - log [4.2×10^{-5}] = **4.38**

24. What is the pH of an aqueous solution if the [H^+] = 7.5×10^{-8}

M? pH = - log [H^+] pH = - log [7.5×10^{-8}] = **7.12**

25. What is the [H+] in a blood sample that has a pH = 3.22?
[H+] = 10^{-pH} [H+] = $10^{-3.22}$ [H+] = **6.03×10^{-4} M**

26. What is the [H+] in a blood sample that has a pH = 7.30?
[H+] = 10^{-pH} [H+] = $10^{-7.30}$ [H+] = **5.01×10^{-8} M**

25. What is the [H^+] in a bleach sample that has a pH = 9.55?

[H+] = 10^{-pH} [H+] = $10^{-9.55}$ [H+] = **$2.82\text{x}10^{-10}$ M**

26. What is the [OH^-] in a seawater sample that has a pH = 8.65?

[H+] = 10^{-pH} [H+] = $10^{-8.65}$ [H+] = $2.24\text{x}10^{-9}$ M

[H+] [OH-] = $1\text{x}10^{-14}$ [$2.24\text{x}10^{-9}$ M] [OH-] = $1\text{x}10^{-14}$ [OH-] = **$4.46\text{x}10^{-9}$ M**

27. What is the [OH^-] in an ammonia solution that has a pH = 10.20?

[H+] = 10^{-pH} [H+] = $10^{-10.20}$ [H+] = $6.31\text{x}10^{-11}$ M

[H+] [OH-] = $1\text{x}10^{-14}$ [$6.31\text{x}10^{-11}$ M] [OH-] = $1\text{x}10^{-14}$ [OH-] = **$1.58\text{x}10^{-4}$ M**

28. What is the [OH^-] in an oven-cleaning solution that has a pH = 12.35?

[H+] = 10^{-pH} [H+] = $10^{-12.35}$ [H+] = $4.47\text{x}10^{-13}$ M

[H+] [OH-] = $1\text{x}10^{-14}$ [$4.47\text{x}10^{-13}$ M] [OH-] = $1\text{x}10^{-14}$ [OH-] = **0.0224 M**

29. What substance is oxidized in the following redox reaction?

Zn(s) + Cu^{2+}(aq) → Zn^{2+}(aq) + Cu(s)

30. What substance is reduced in the following redox

reaction? Co(s) + 2 ***H***Cl(aq) → $CoCl_2$(aq) + H_2(g)

31. What substance is oxidized in the following redox reaction?

F_2(g) + 2 ***Br^-***(aq) → 2 F^-(aq) + Br_2(l)

32. What substance is oxidized in the following redox reaction?

$HgCl_2$(aq) + ***Sn^{2+}***(aq) → Sn^{4+}(aq) + Hg_2Cl_2(s) + Cl^-(aq)

33. What substance is reduced in the following redox reaction?

H^+(aq) + Fe(s) + ***N***O_3^-(aq) → Fe^{3+}(aq) + NO(aq) + H_2O(l)

Sample Chemistry Question (Ch. 15, 16, 17) - CH 223

Questions for Chapters Seventeen Part II, Nineteen and Twenty:

1. What is the concentration of F^- in a saturated solution of BaF_2 if $K_{sp} = 1.7*10^{-6}$?

   a. $7.5*10^{-3}$ M
   b. $8.2*10^{-4}$ M
   c. $1.5*10^{-2}$ M
   d. $4.3*10^{-7}$ M
   e. $1.5*10^{-6}$ M

2. For $BaSO_4$, $K_{sp} = 1.1*10^{-10}$. What is the molar solubility of $BaSO_4$ in a solution which is 0.018 M in Na_2SO_4?

   a. 0.018 M
   b. $7.8*10^{-5}$ M
   c. $1.1*10^{-5}$ M
   d. $6.1*10^{-9}$ M
   e. $1.1*10^{-10}$ M

3. In which of the following reactions do you expect to have the largest increase in entropy?

   a. $I_{2(s)} \rightarrow I_{2(g)}$
   b. $2\ IF_{(g)} \rightarrow I_{2(g)} + F_{2(g)}$
   c. $Mn_{(s)} + O_{2(g)} \rightarrow MnO_{2(s)}$
   d. $Hg_{(l)} + S_{(s)} \rightarrow HgS_{(s)}$
   e. $CuSO_{4(s)} + 5\ H_2O_{(l)} \rightarrow CuSO_4 \cdot 5H_2O_{(s)}$

4. For a particular reaction the equilibrium constant is $1.50*10^{-2}$ at 370 °C. ΔH° is +16.0 kJ. What is ΔS° for the reaction?

   a. -18.8 J/K
   b. +18.8 J/K
   c. -10.0 J/K
   d. +10.0 J/K
   e. None of the above

5. How many electrons are transferred in the following reaction:
   $\mathbf{2\ ClO_3^- + 12\ H^+ + 10\ I^- \rightarrow 5\ I_2 + Cl_2 + 6\ H_2O}$

   a. 12
   b. 5
   c. 2
   d. 30
   e. 10

6. If a current of 6.0 amps is passed through a solution of $Ag^+_{(aq)}$ for 1.5 hours, how many grams of silver are produced?

a. 0.60 g
b. 36 g
c. 0.34 g
d. 3.0 g
e. 1.0 g

Here are the answers to the previous questions:

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1. What is the concentration of F^- in a saturated solution of BaF_2 if $K_{sp} = 1.7*10^{-6}$?

a. $7.5*10^{-3}$ M
b. $8.2*10^{-4}$ M
c. $1.5*10^{-2}$ M
d. $4.3*10^{-7}$ M
e. $1.5*10^{-6}$ M

Answer: Recall that the K_{sp} expression can be written as $K_{sp} = [Ba^{2+}][F^-]^2$ for BaF_2. One mole of BaF_2 creates two moles of F^- and one mole of Ba^{2+} per mol of BaF_2 dissolved. If x represents the amount of Ba^{2+} dissolved, then 2x represents the F^-, and we can re-write the K_{sp} expression as $K_{sp} = 1.7*10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$. x represents the solubility of the BaF_2, and here $x = (1.7*10^{-6}/4)^{1/3} = 7.5*10^{-3}$ M. The concentration of $[F^-]$ will be twice as much as the solubility (since there are two F^- ions per BaF_2 molecule); hence, the concentration of F^- in a saturated BaF_2 solution will be $2(7.5*10^{-3}$ M) = **$1.5*10^{-2}$ M**, answer **c**.

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2. For $BaSO_4$, $K_{sp} = 1.1*10^{-10}$. What is the molar solubility of $BaSO_4$ in a solution which is 0.018 M in Na_2SO_4?

a. 0.018 M
b. $7.8*10^{-5}$ M
c. $1.1*10^{-5}$ M
d. $6.1*10^{-9}$ M
e. $1.1*10^{-10}$ M

Answer: If we have a 0.018 M Na_2SO_4 solution, we have, therefore, a solution with $[SO_4^{2-}] = 0.018$ M and $[Na^+] = 0.036$ M.

K_{sp} for $BaSO_4 = [Ba^{2+}][SO_4^{2-}]$, and normally we would write $K_{sp} = x*x$ since both ions dissociate in a 1:1 ratio. x here is the solubility of the $BaSO_4$.

Here, however, we have a common ion present - namely sulfate. We can re-write the equation for K_{sp} as following:

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (x)(x+0.018)$ since the sulfate has contributions from both the $BaSO_4$ and the Na_2SO_4.

Normally x is much smaller than 0.018, and (x+0.018) will likely be approximately equal to 0.018 using significant figures. We can re-write the equation as:

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (x)(x+0.018) = (x)(0.018)$

Solving for x gives the solubility: $x = K_{sp}/0.018 = 1.1*10^{-10}/0.018 = 6.1*10^{-9}$

Note that x is much less than 0.018, making the assumption valid. Answer = **$6.1*10^{-9}$**, answer **d**.

---

3. In which of the following reactions do you expect to have the largest increase in entropy?

    a. $I_{s(s)} \rightarrow I_{2(g)}$
    b. $2\ IF_{(g)} \rightarrow I_{2(g)} + F_{2(g)}$
    c. $Mn_{(s)} + O_{2(g)} \rightarrow MnO_{2(s)}$
    d. $Hg_{(l)} + S_{(s)} \rightarrow HgS_{(s)}$
    e. $CuSO_{4(s)} + 5\ H_2O_{(l)} \rightarrow CuSO_4 \cdot 5H_2O_{(s)}$

Answer: Entropy will increase upon an increase in disorder. This can occur through several methods, including solids going to liquids and/or liquids going to gases. Another disorder enhancement comes about when a large molecule splits into many particles.

Option a shows a solid going to a gas. This would increase disorder; hence, this would increase the entropy.

Option b shows two gas molecules rearranging to make two more gas molecules. There is no disorder here except possibly in the fact that a mixed molecule (IF) is dissociating to "pure" elements (I_2 and F_2), which might lead to a decrease in entropy (less randomness in the elements than in the molecules.) Hence, this option will probably lead to a decrease in entropy instead of an increase.

Option c has a solid and gas combining to make a solid. Anytime gases become solids there is usually a decrease in entropy, not an increase. Also, two molecules are changing into one product: this is less disorder, and a lowering of entropy.

Option d is similar to option c except that a liquid is being forced to become a solid. This will also lead to a decrease in entropy. Also, two molecules are changing into one product: this is less disorder, and a lowering of entropy.

Option e is similar to option d in that a liquid is being turned into a solid. Note also how six reactant molecules are converting to one product molecule: this is a more ordered product state, which defeats entropy. Entropy will diminish here.

The only option which should increase the entropy is option **a**, the correct **answer** for this problem.

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4. For a particular reaction the equilibrium constant is $1.50*10^{-2}$ at 370 °C. ΔH° is +16.0 kJ. What is ΔS° for the reaction?

    a. -18.8 J/K
    b. +18.8 J/K
    c. -10.0 J/K
    d. +10.0 J/K
    e. None of the above

Answer: To solve this problem we need two equations: $\Delta G = \Delta H - T\Delta S$, and $\Delta G = -RT \ln K$. Combining the equations leads to:

$\Delta G = \Delta H - T\Delta S = -RT \ln K$, or

$\Delta S = (RT \ln K + \Delta H)/T$

Converting °C to K and kJ to J gives:

$\Delta S = ((8.314 * 643\ K) \ln (1.50*10^{-2}) + (16.0*10^{3}\ J))/643\ K =$ **-10.0 J/K**, answer **c**.

---

5. How many electrons are transferred in the following reaction:

$2\ ClO_3^- + 12\ H^+ + 10\ I^- \rightarrow 5\ I_2 + Cl_2 + 6\ H_2O$

a. 12
b. 5
c. 2
d. 30
e. 10

Answer: To solve this equation, we need to break the oxidizing and reducing portions into half reactions. Cl in chlorate changes its oxidation number upon going to Cl_2; I^- also changes its oxidation number upon going to I_2.

For the Cl:

$12\ H^+ + 2\ ClO_3^- \rightarrow Cl_2 + 6\ H_2O$

gives a balanced reaction for mass, but not for charge. The product side has no charge, the reactant side has a net +10 charge; hence, add 10 electrons to the reactant side to balance charge. The result:

$10\ e^- + 6\ H^+ + 2\ ClO_3^- \rightarrow Cl_2 + 3\ H_2O$

For the I^- side,

$2\ I^- \rightarrow I_2$

This equation is balanced for mass, but not charge: the reactant side has a net -2 charge, and the product side has no charge. Add 2 electrons to balance the equation for both mass and charge to get:

$2\ I^- \rightarrow I_2 + 2\ e^-$

We can now clearly see that the I^- is being oxidized (losing electrons) and the ClO_3^- is being reduced (gaining electrons.)

To balance the reaction, multiple the I^- equation by five to cancel the electrons. This results in ten net electrons being transferred from the I^- to the ClO_3^-, meaning that **10 electrons are being transferred**, answer **e**.

6. If a current of 6.0 amps is passed through a solution of $Ag^+_{(aq)}$ for 1.5 hours, how many grams of silver are produced?

a. 0.60 g
b. 36 g
c. 0.34 g
d. 3.0 g
e. 1.0 g

Answer: Remember that an amp equals a Coulomb per second. In addition, the Faraday (96485 C/mol e^-) will be helpful, and each Ag^+ will need one electron to become $Ag_{(s)}$. Unit analysis will help to solve this problem:

6.0 amps = 6.0 C/s * (60 s/minute) * (60 minutes/hour) * 1.5 hours = 32400 C delivered to the Ag^+.

To find out the quantity of silver produced, use the Faraday constant and the atomic mass of silver.

32400 C * (mol e^- / 96485 C) * (mol Ag^+ / mol e^-) * (108 g Ag / mol Ag) = **36 g** of silver, answer **b**.

Nomenclature of Coordination Complexes

(Self quiz after overview) *Overview:* Ligands = attached atoms or molecules

Anion Name	*Ligand Name*
Bromide, Br^-	Bromo
Carbonate, CO_3^{2-}	Carbonato
Chloride, Cl^-	Chloro
Cyanide, CN^-	Cyano
Fluoride, F^-	Fluoro
Hydroxide, OH^-	Hydroxo
Oxalate, $C_2O_4^{2-}$	Oxalato
EDTA	Ethylenediamine tetracetato

Neutral Ligand	*Ligand Name*
Ammonia, NH3	Ammine
Water, H2O	Aqua
Carbon Monoxide, CO	Carbonyl
Ethylenediamine, en	Ethylenediamine

Metal	*Anion Name*
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Manganese	Manganate
Nickel	Nickelate
Platinum	Platinate
Zinc	Zincate

If more than one ligand is attached then,

2 = di
3 = tri
4 = tetra
5 = penta
6 = hexa

If the ligand has di, tri, tetra, in its name or is a dentate molecule, and you want to indicate you have more than one of them then use,

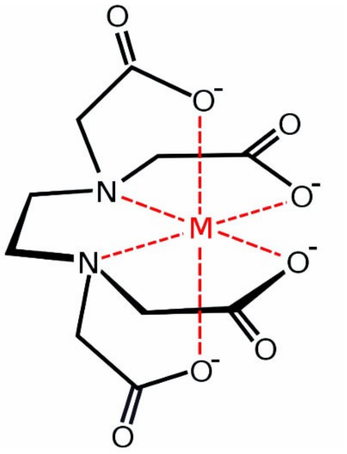
2 = bis
3= tris
4 = tetrakis

The Dentates

Bidentates – two bites
- Oxalate (ox)
- Ethylenediamine (en)
- Malate (mal)

Tridentate – three bites
- Citrate (cit)

Hexadentate – six bites
- EDTA



EDTA wrapped around a metal ion.

How to name complex ions that are positively charged.

The name of the transition metal comes at the end of the name along with a Roman numeral indicating its charge,

Ex: $Co(NH_3)_6^{3+}$ = hexamminecobalt(III)
$Fe(H_2O)_6^{2+}$ = hexaquairon(II)
$Ni(en)_2^{2+}$ = bis(ethylenediamine)nickel(II)
$Cu(CO)_4$ = tetracarbonylcopper(II)

Now, every compound has both a positive part and a negative part, like NaCl is really Na^+ and Cl^-. The same is true for complex ions only the positive and negative parts can be really large and complex (which is why they are called complex ions).

In the above examples I gave several positive ions and their name, but each of them also has a negative part that goes with them. Consider the following compounds,

Ex: $Co(NH_3)_6Cl_3$ = hexamminecobalt(III) chloride
$Fe(H_2O)_6(OH)_2$ = hexaquairon(II) hydroxide
$Ni(en)_2SO_4$ = bis(ethylenediamine)nickel(II) sulfate
$Cu(CO)_4CO_3$ = tetracarbonylcopper(II) carbonate

In each case an anion has been added to the complex ion. This completes the structure and produces an overall neutral compound that could be stored in a bottle in our storeroom. You will notice that the nomenclature has not changed much from what we learned about transition metal nomenclature, you name the metal ion, indicate its charge with a Roman Numeral, and then add the anion onto the end. Only in this case the positive ion is large and complex but the nomenclature is the same.

How to name complex ions that are negatively charged

A large number of complex ions are negatively charged. This is caused by having several negatively charged ligands attached to the metal. Consider the following compounds,

Ex: $CoCl_6^{3-}$ = Co^{3+} with 6 Cl^-
$Fe(CN)_6^{3-}$ = Fe^{3+} with 6 CN^-
$Cr(OH)_4^-$ = Cr^{3+} with 4 OH^-
$RhBr_4^{2-}$ = Rh^{2+} with 4 Br^-

When a complex is negative the name of the metal changes. Generally we use its actual name (iron becomes ferrium) and we add an –ate at the end of its name. So $Fe(CN)_6^{3-}$ becomes hexacyanoferrate(III). Therefore, from the example given above we get the following names;

Ex: $CoCl_6^{3-}$ = hexachlorocobaltate(III)
$Fe(CN)_6^{3-}$ = hexacyanoferrate(III)
$Cr(OH)_4^-$ = tetrahydroxochromate(III)
$RhBr_4^{2-}$ = tetrabromorhodate(II)

Of course, once again, negative ions are never found without a corresponding positive ion. So the compounds above would actually look something like this,

Ex: Na_3CoCl_6 = Sodium Hexachlorocobaltate(III)
$K_3Fe(CN)_6$ = Potassium Hexacyanoferrate(III)
$LiCr(OH)_4$ = Lithium Tetrahydroxochromate(III)
$CaRhBr_4$ = Calcium Tetrabromorhodate(II)

Problems

1) Name the following compounds,

$Cu(OH)_4^{2-}$

Na_3AuCl_4

$Mo(CN)_6^{4-}$

$Fe(CO)_6ScCl_6$

$[Cr(NH_3)_3(H_2O)_3]Cl_3$

$[Pt(NH_3)_5Cl]Br_3$

$[Pt(en)_2Cl_2]Cl_2$

$[Co(en)_3]_2(SO_4)_3$

$K_4[Fe(CN)_6]$

$Na_2[NiCl_4]$

$Pt(NH_3)_2Cl_4$

$(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$

$[Ag(NH_3)_2][Ag(CN)_2]$

$[CoBr(NH_3)_5]SO_4$

$[Fe(NH_3)_6][Cr(CN)_6]$

$[Co(SO_4)(NH_3)_5]^+$

$[Fe(OH)(H_2O)_5]^{2+}$

2) Write the formula of the following coordination compounds.

hexaammineiron(III) nitrate

ammonium tetrachlorocuprate(II)

sodium monochloropentacyanoferrate(III)

potassium hexafluorocobaltate(III)

3) Give the number of d electrons for each of the complexes listed below. Are the complexes paramagnetic or diamagnetic?

	# d electrons	Paramagnetic or Diamagnetic
$\mathrm{Pd(NH_3)_2Cl}$		
$\mathrm{Ru(CO)_6^{3+}}$		
$\mathrm{Ni(H_2O)_6^{2+}}$		
$\mathrm{HgCl_4^{2-}}$		

Answer Key

1) Name the following compounds,

$Cu(OH)_4^{2-}$	tetrahydoxocuprate(II)
Na_3AuCl_4	Sodium tetrachloroaurate(I)
$Mo(CN)_6^{4-}$	hexacyanomolybdenate(II)
$Fe(CO)_6ScCl_6$	hexacarbonyliron(III) hexachloroscanadate(III)
$[Cr(NH_3)_3(H_2O)_3]Cl_3$	triamminotriaquachromium(III) chloride
$[Pt(NH_3)_5Cl]Br_3$	pentaamminochloroplatinum(IV) bromide
$[Pt(en)_2Cl_2]Cl_2$	dichlorobis(ethylenediamine)platinum(II) chloride
$[Co(en)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(III) sulfate
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$Na_2[NiCl_4]$	Sodium tetrachloronickelate(II)
$Pt(NH_3)_2Cl_4$	diamminoplatinum(IV) chloride
$(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$	Ammonium diaquabis(oxalate)nickelate(II)
$[Ag(NH_3)_2][Ag(CN)_2]$	diamminosilver(I) dicyanoargentate(I)
$[CoBr(NH_3)_5]SO_4$	pentamminobromocobalt(III) sulfate
$[Fe(NH_3)_6][Cr(CN)_6]$	hexamminoiron(III) hexacyanochromate(III)
$[Co(SO_4)(NH_3)_5]^+$	pentamminosulfatocobalt(III)
$[Fe(OH)(H_2O)_5]^{2+}$	pentaaquahydroxoiron(III)

2) Write the formula of the following coordination compounds.

hexaammineiron(III) nitrate	$Fe(NH_3)_6(NO_3)_3$
ammonium tetrachlorocuprate(II)	$(NH_4)_2CuCl_4$
sodium monochloropentacyanoferrate(III)	$Na_3Fe(CN)_5Cl$
potassium hexafluorocobaltate(III)	K_3CoF_6

3) Give the number of d electrons for each of the complexes listed below. Are the complexes paramagnetic or diamagnetic?

	# d electrons	Paramagnetic or Diamagnetic
$Pd(NH_3)_2Cl$	d8	Diamagnetic
$Ru(CO)_6^{3+}$	d5	Paramagnetic
$Ni(H_2O)_6^{2+}$	d8	Paramagnetic
$HgCl_4^{2-}$	d10	Diamagnetic

CH 223

Sample Quiz #1 Name: ____ Lab Section: _______

Be sure to show all work, use the correct number of significant figures, circle final answers and use correct units in all problems.

---

1. For the reaction: **$CH_4(g) + 2\ O_2(g) \rightleftharpoons CO_2(g) + 2\ H_2O(g)$, $K_c = 1.15*10^7$** (430. K), held within a 2.00 L flask (10 points)

   Write the equilibrium constant expression for K_c.

   Is the reaction at equilibrium if $[CO_2] = [H_2O] = 0.00350$ M, $[O_2] = 3.31*10^{-6}$ M and $[CH_4] = 3.31*10^{-6}$ M? If not, indicate the direction that the reaction must proceed to achieve equilibrium.

   What is the value of the equilibrium constant if the reaction is $2\ CH_4(g) + 4\ O_2(g) \rightleftharpoons 2\ CO_2(g) + 4\ H_2O(g)$ at 430. K?

   What is the value of K_c at 430. K for the reaction: $CO_2(g) + 2\ H_2O(g) \rightleftharpoons CH_4(g) + 2\ O_2(g)$

2. For the reaction: **$Cl_2(g) + Br_2(g) \rightleftharpoons 2\ BrCl(g)$, $K_c = 10.3$** (150 °C) (4 points)

   Is this reaction product-favored or reactant-favored?

   If 0.500 mol BrCl in a 1.00 L flask is allowed to reach equilibrium, what are the equilibrium concentrations of Cl_2, Br_2 and BrCl?

3. For the reaction: **$RX(s) \rightleftharpoons R(g) + X(g)$, $K_c = 1.11*10^{-7}$** (200. K) (6 points)

   Write the equilibrium constant expression.

   Calculate the equilibrium concentrations of R and X if a solid sample of RX is placed in a closed vessel and decomposes until equilibrium is established.

   What is the value of **K_p** at 200. K?

CH 223
Sample Quiz #1 Name: ____ Lab Section: _______
Answers

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1. For the reaction: **$CH_4(g) + 2\ O_2(g) \rightleftharpoons CO_2(g) + 2\ H_2O(g)$, $K_c = 1.15*10^7$** (430. K), held within a 2.00 L flask (10 points)

   Write the equilibrium constant expression for K_c. **$K_c = [H_2O]^2[CO_2]/[CH_4][O_2]^2 = 1.15 \text{ x } 10^7$**

   Is the reaction at equilibrium if $[CO_2] = [H_2O] = 0.00350$ M, $[O_2] = 3.31*10^{-6}$ M and $[CH_4] = 3.31*10^{-6}$ M? If not, indicate the direction that the reaction must proceed to achieve equilibrium.

   $Q = 1.18 \text{ x } 10^9$
   Q > K, will shift left (to reactant side)

   What is the value of the equilibrium constant if the reaction is $2\ CH_4(g) + 4\ O_2(g) \rightleftharpoons 2\ CO_2(g) + 4\ H_2O(g)$ at 430. K?

   $K_{new} = 1.32 \text{ x } 10^{14}$

   What is the value of K_c at 430. K for the reaction: $CO_2(g) + 2\ H_2O(g) \rightleftharpoons CH_4(g) + 2\ O_2(g)$

   $K_{new} = 8.70 \text{ x } 10^{-8}$

2. For the reaction: **$Cl_2(g) + Br_2(g) \rightleftharpoons 2\ BrCl(g)$, $K_c = 10.3$** (150 °C) (4 points)

   Is this reaction product-favored or reactant-favored? **product favored ($K_c > 1$)**

   If 0.500 mol BrCl in a 1.00 L flask is allowed to reach equilibrium, what are the equilibrium concentrations of Cl_2, Br_2 and BrCl?

   $[Cl_2] = [Br_2] = 0.0960$ M
   $[BrCl] = 0.308$ M

3. For the reaction: **$RX(s) \rightleftharpoons R(g) + X(g)$, $K_c = 1.11*10^{-7}$** (200. K) (6 points)

   Write the equilibrium constant expression. **$K_c = [R][X] = 1.11 \text{ x } 10^{-7}$**

   Calculate the equilibrium concentrations of R and X if a solid sample of RX is placed in a closed vessel and decomposes until equilibrium is established.

   $[R] = [X] = 3.33 \text{ x } 10^{-4}$ M

   What is the value of **K_p** at 200. K?

   $K_p = 2.99 \text{ x } 10^{-5}$

CH 223
Sample Quiz #2 Name: ____ Lab Section: _______

Be sure to show all work, use the correct number of significant figures, circle final answers and use correct units in all problems.

---

1. For the equilibrium **$2\ CO_{(g)} + O_{2(g)} \rightleftharpoons 2\ CO_{2(g)}$** where **$\Delta H < 0$**, how will each of the following affect the equilibrium? Circle the correct answer. (4 points)

   a. Oxygen is added to the system. **right left no change**

   b. The reaction mixture is heated. **right left no change**

   c. The pressure of the reaction mixture is increased. **right left no change**

   d. CO_2 is removed from the system. **right left no change**

2. Complete and balance the following acid-base reactions. Identify the acid, base, conjugate acid and conjugate base in each reaction. Predict whether the equilibrium lies predominantly to the left or the right. (6 points)

   a. $HBr + NH_3 \rightarrow$

   b. $HOCl + H_2O \rightarrow$

3. What is the pH of a 0.116 M $Mg(OH)_2$ solution? Assume $Mg(OH)_2$ is a strong base. (3 points)

4. My soft drink has a pH of 6.22. Is the soft drink acidic, alkaline or neutral? Calculate the hydronium and hydroxide ion concentration in the soft drink. (3 points)

5. Benzoic acid, C_6H_5COOH, is a weak acid ($K_a = 6.28*10^{-5}$). If I dissolve 1.22 g of C_6H_5COOH in enough water to make 500. mL of solution, what is the resulting pH of the solution? (4 points)

CH 223
Sample Quiz #2 Name: ______________________________ Lab Section: _______
Answers

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1. For the equilibrium $\mathbf{2\,CO_{(g)} + O_{2(g)} \rightleftharpoons 2\,CO_{2(g)}}$ where $\mathbf{\Delta H < 0}$, how will each of the following affect the equilibrium? Circle the correct answer. (4 points)

   a. Oxygen is added to the system. [✓ **right**] **left** **no change**

   b. The reaction mixture is heated. **right** [✓ **left**] **no change**

   c. The pressure of the reaction mixture is increased. [✓ **right**] **left** **no change**

   d. CO_2 is removed from the system. [✓ **right**] **left** **no change**

2. Complete and balance the following acid-base reactions. Identify the acid, base, conjugate acid and conjugate base in each reaction. Predict whether the equilibrium lies predominantly to the left or the right. (6 points)

   a. $HBr + NH_3 \rightarrow \mathbf{NH_4^+ + Br^{-1}}$ **RIGHT (SA)**
   SA WB CA CB

   b. $HOCl + H_2O \rightarrow \mathbf{OCl^{-1} + H_3O^{+1}}$ **LEFT (WA)**
   WA WB CB CA

3. What is the pH of a 0.116 M $Mg(OH)_2$ solution? Assume $Mg(OH)_2$ is a strong base. (3 points)

   pH = 13.365

4. My soft drink has a pH of 6.22. Is the soft drink acidic, alkaline or neutral? Calculate the hydronium and hydroxide ion concentration in the soft drink. (3 points)

   Acidic!
   $\mathbf{[H_3O^+] = 6.0 \times 10^{-7}\ M}$
   $\mathbf{[OH^{-1}] = 1.7 \times 10^{-8}\ M}$

5. Benzoic acid, C_6H_5COOH, is a weak acid ($K_a = 6.28 \times 10^{-5}$). If I dissolve 1.22 g of C_6H_5COOH in enough water to make 500. mL of solution, what is the resulting pH of the solution? (4 points)

   pH = 2.951

CH 223
Sample Quiz #3 Name: ____ Lab Section: _______

Be sure to show all work, use the correct number of significant figures, circle final answers and use correct units in all problems.

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1) Acetic acid (CH_3CO_2H, 2.00 g) and sodium acetate ($NaC_2H_3O_2$, 2.00 g) are dissolved in enough water to make 1.00 L of solution. Calculate the pH of the solution ($K_a = 1.80 * 10^{-5}$) (6 points)

2) 50.0 mL of 0.150 M acetic acid is being titrated with 0.250 M LiOH. What is the pH at the half-equivalence point? How many mL of LiOH are required to reach the half equivalence point? ($K_a = 1.80 * 10^{-5}$) (4 points)

3) A solution contains 20.0 mL of 0.150 M HNO_3. (10 points)

a) What is the pH of the HNO_3 solution?

b) What is the pH after 10.0 mL of 0.250 M NaOH has been added?

c) What is the pH at the equivalence point? How many mL of 0.250 M NaOH need to be added to reach the equivalence point?

d) What is the pH after 30.0 mL of 0.250 M NaOH have been added?

CH 223
Sample Quiz #3 Name: ____ Lab Section: _______
Answers

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1) Acetic acid (CH_3CO_2H, 2.00 g) and sodium acetate ($NaC_2H_3O_2$, 2.00 g) are dissolved in enough water to make 1.00 L of solution. Calculate the pH of the solution ($K_a = 1.80 * 10^{-5}$) (6 points)

pH = 4.609

2) 50.0 mL of 0.150 M acetic acid is being titrated with 0.250 M LiOH. What is the pH at the half-equivalence point? How many mL of LiOH are required to reach the half equivalence point? ($K_a = 1.80 * 10^{-5}$) (4 points)

pH = 4.745
V (LiOH) = 15.0 mL

3) A solution contains 20.0 mL of 0.150 M HNO_3. (10 points)

a) What is the pH of the HNO_3 solution?

pH = 0.824

b) What is the pH after 10.0 mL of 0.250 M NaOH has been added?

pH = 1.78

c) What is the pH at the equivalence point? How many mL of 0.250 M NaOH need to be added to reach the equivalence point?

pH = 7
V (NaOH) = 12.0 mL

d) What is the pH after 30.0 mL of 0.250 M NaOH have been added?

pH = 12.954

CH 223
Sample Quiz #4 Name: ____ Lab Section: _______

Be sure to show all work, use the correct number of significant figures, circle final answers and use correct units in all problems.

Question #1: 10 points

a. Write the balanced equation for the equilibrium of copper(II) hydroxide, $Cu(OH)_2$, in water and the K_{sp} expression. $K_{sp} = 2.2*10^{-20}$ at 25 ˚C.

b. What is the solubility of copper(II) hydroxide at 25 ˚C?

c. What is the solubility of copper(II) hydroxide at 25 ˚C if the initial $[Cu^{+2}] = 0.010$ M?

d. Will a precipitate form when 10.0 mL of 0.0015 M copper(II) nitrate is mixed with 10. mL of 0.015 M sodium hydroxide?

Question #2: 4 points

Given the following reactions,

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^{-1}(aq)$ $K_{sp} = 5.4 \times 10^{-13}$
$Ag^+(aq) + 2\ CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$ $K_f = 1.2 \times 10^{21}$

determine the equilibrium constant for the reaction below.

$AgBr(s) + 2\ CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq) + Br^{-1}(aq)$

Question #3: 6 points

a. A solution of Na_2SO_4 is added dropwise to a solution that is 0.010 M Ba^{2+} and 0.010 M Ag^{+1}. Neglecting volume changes, which salt precipitates first, $BaSO_4$ ($K_{sp} = 1.1*10^{-10}$) or Ag_2SO_4 ($K_{sp} = 1.7*10^{-5}$)?

b. What is the concentration of the cation that precipitates first when the second cation begins to precipitate?

CH 223
Sample Quiz #4 Name: ____ Lab Section: _______
Answers

Question #1: 10 points

a. Write the balanced equation for the equilibrium of copper(II) hydroxide, $Cu(OH)_2$, in water and the K_{sp} expression. $K_{sp} = 2.2*10^{-20}$ at 25 ˚C.

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\ OH^{-1}(aq)$
$K_{sp} = [Cu^{2+}][OH^{-1}]^2$

b. What is the solubility of copper(II) hydroxide at 25 ˚C?

$x = 1.8 \times 10^{-7}$ M

c. What is the solubility of copper(II) hydroxide at 25 ˚C if the initial $[Cu^{+2}] = 0.010$ M?

$x = 7.5 \times 10^{-10}$ M *(7.4×10^{-10} ok)*

d. Will a precipitate form when 10.0 mL of 0.0015 M copper(II) nitrate is mixed with 10. mL of 0.015 M sodium hydroxide?

Yes, solid forms

Question #2: 4 points

Given the following reactions,

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^{-1}(aq)$ $K_{sp} = 5.4 \times 10^{-13}$
$Ag^+(aq) + 2\ CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$ $K_f = 1.2 \times 10^{21}$

determine the equilibrium constant for the reaction below.

$AgBr(s) + 2\ CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq) + Br^{-1}(aq)$

$K_{net} = 6.5 \times 10^8$

Question #3: 6 points

a. A solution of Na_2SO_4 is added dropwise to a solution that is 0.010 M Ba^{2+} and 0.010 M Ag^{+1}. Neglecting volume changes, which salt precipitates first, $BaSO_4$ ($K_{sp} = 1.1*10^{-10}$) or Ag_2SO_4 ($K_{sp} = 1.7*10^{-5}$)?

$BaSO_4$ precipitates first

b. What is the concentration of the cation that precipitates first when the second cation begins to precipitate?

6.5×10^{-10} M

CH 223
Sample Quiz #5 Name: ____ Lab Section: _______

Be sure to show all work, use the correct number of significant figures, circle final answers and use correct units in all problems.

Question #1: (10 points) This reaction was studied at 25.0 °`C: **$P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(l)$**
Use the data acquired to **calculate values for ΔH°_{rxn}, ΔS°_{rxn}** and finally **ΔG°_{rxn}.**

Species	ΔH_f°(kJ/mol)	S°(J/K· mol)
$P_4O_{10}(s)$	–2984.0	228.9
$H_2O(l)$	–285.8	69.95
$H_3PO_4(l)$	–1279.0	110.5

Question #2: (5 points) One kind of battery used in watches contains mercury(II) oxide. As current flows, the mercury(II) oxide is reduced to mercury: **$HgO(s) + H_2O(l) + 2\ e^- \rightarrow Hg(l) + 2\ OH^-(aq)$**

If 2.3×10^{-5} amperes flows continuously for 1200 days, what mass of $Hg(l)$ is produced?

Question #3: (5 points) Write a balanced chemical equation for the following reaction in an **acidic** solution.

$Cr_2O_7^{2-}(aq) + Ni(s) \rightarrow Cr^{3+}(aq) + Ni^{2+}(aq)$

CH 223
Sample Quiz #5 Name: ____ Lab Section: _______
Answers

Question #1: (10 points) This reaction was studied at 25.0 °C: **$P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(l)$**

Use the data acquired to **calculate values for $\Delta H°_{rxn}$, $\Delta S°_{rxn}$** and finally **$\Delta G°_{rxn}$.**

Species	$\Delta H_f°$(kJ/mol)	$S°$(J/K· mol)
$P_4O_{10}(s)$	–2984.0	228.9
$H_2O(l)$	–285.8	69.95
$H_3PO_4(l)$	–1279.0	110.5

ΔH_{rxn} = -417.2 kJ/mol

ΔS_{rxn} = -206.6 J/mol

ΔG_{rxn} = -355.6 kJ/mol

Question #2: (5 points) One kind of battery used in watches contains mercury(II) oxide. As current flows, the mercury(II) oxide is reduced to mercury: **$HgO(s) + H_2O(l) + 2\ e^- \rightarrow Hg(l) + 2\ OH^-(aq)$**

If 2.3×10^{-5} amperes flows continuously for 1200 days, what mass of Hg(l) is produced?

2.5 g Hg

Question #3: (5 points) Write a balanced chemical equation for the following reaction in an **acidic** solution.

$Cr_2O_7^{2-}(aq) + Ni(s) \rightarrow Cr^{3+}(aq) + Ni^{2+}(aq)$

$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 3\ Ni(s) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l) + 3\ Ni^{2+}(aq)$

CH 223
Sample Quiz #6 Name: ____ Lab Section: _______

Be sure to show all work, use the correct number of significant figures, circle final answers and use correct units in all problems.

Question #1: (10 points total, 2 points each)

- Circle the ion(s) with a $[\mathrm{Ar}]3d^5$ electron configuration: Co^{2+} Mn^{2+} Fe^{3+}?
- Identify the neutral element with the ground state electron configuration $[\mathrm{Xe}]4f^{14}5d^{6}6s^{2}$. ___________________
- What is the highest oxidation state for chromium? ___________________
- What is the oxidation state of iron in $K_4[Fe(CN)_6]$? ___________________
- List a possible geometry of a metal complex with a coordination number of four: ___________________

Question #2: (10 points) Provide the right name or formula for the coordination compounds below.

Name	Formula
	$[Cr(en)_2(H_2O)_2]SO_4$
hexacarbonylruthenium(III) perchlorate	
dicyanobis(ethylenediamine)zirconium(IV) nitrate	
	$(NH_4)_2[Cu(CN)_4]$
potassium tetrachloroplatinate(II)	

CH 223
Sample Quiz #6 Name: ____ Lab Section: _______
Answers

Question #1: (10 points total, 2 points each)

- Circle the ion(s) with a [Ar]3d^5 electron configuration: Co^{2+} [✓ **Mn^{2+}**] [✓ **Fe^{3+}**]?
- Identify the neutral element with the ground state electron configuration [Xe]4f^{14}5$d^6$6s^2. **osmium**
- What is the highest oxidation state for chromium? **+6**
- What is the oxidation state of iron in $K_4[Fe(CN)_6]$? **+2**
- List a possible geometry of a metal complex with a coordination number of four: **tetrahedral** *or* **square planar**

Question #2: (10 points) Provide the right name or formula for the coordination compounds below.

Name	Formula
diaquabis(ethylenediammine)chromium(II) sulfate	$[Cr(en)_2(H_2O)_2]SO_4$
hexacarbonylruthenium(III) perchlorate	**$[Ru(CO)_6](ClO_4)_3$**
dicyanobis(ethylenediamine)zirconium(IV) nitrate	**$[Zr(CN)_2(en)_2](NO_3)_2$**
ammonium tetracyanocuprate(II)	$(NH_4)_2[Cu(CN)_4]$
potassium tetrachloroplatinate(II)	**$K_2[PtCl_4]$**

CH 223 Sample Exam
Exam I Name: ______________________________ Lab Section: ______

Part I: Multiple Choice Questions (100 Points) There is *only* one best answer for each question.

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1. Write the expression for K for the reaction: $\mathbf{Al_2S_3(s) \rightleftharpoons 2\ Al^{3+}(aq) + 3\ S^{2-}(aq)}$

a. $K = [Al^{3+}]^2[S^{2-}]^3$
b. $K = [Al^{3+}][S^{2-}]$
c. $K = [2\ Al^{3+}][3\ S^{2-}]$
d. $K = \dfrac{[Al_2S_3]}{[Al^{3+}]^2[S^{2-}]^3}$
e. $K = \dfrac{[Al^{3+}]^2[S^{2-}]^3}{[Al_2S_3]}$

2. Write the expression for K_p for the reaction: $\mathbf{2\ HBr(g) \rightleftharpoons H_2(g) + Br_2(l)}$

a. $K_p = \dfrac{P_{HBr}^2}{P_{Br_2}P_{H_2}}$
b. $K_p = \dfrac{P_{H_2}}{P_{HBr}^2}$
c. $K_p = P_{HBr}^2$
d. $K_p = \dfrac{P_{HBr}^2}{P_{H_2}}$
e. $K_p = \dfrac{P_{H_2}P_{Br_2}}{P_{HBr}^2}$

3. A 4.00 L flask is filled with 0.75 mol SO_3, 2.50 mol SO_2, and 1.30 mol O_2, and allowed to reach equilibrium. Predict the effect on the concentrations of SO_3 as equilibrium is achieved by using Q, the reaction quotient. Assume the temperature of the mixture is chosen so that $K_c = 12$. $\mathbf{2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)}$

a. $[SO_3]$ will decrease because $Q > K$.
b. $[SO_3]$ will decrease because $Q < K$.
c. $[SO_3]$ will increase because $Q < K$.
d. $[SO_3]$ will increase because $Q > K$.
e. $[SO_3]$ will remain the same because $Q = K$.

4. This reaction below is studied at a high temperature. $\mathbf{PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)}$ At equilibrium, the partial pressures of the gases are as follows: $PCl_5 = 1.8 \times 10^{-2}$ atm, $PCl_3 = 5.6 \times 10^{-2}$ atm, and $Cl_2 = 3.8 \times 10^{-4}$ atm. What is the value of K_p for the reaction?

a. 3.8×10^{-7}
b. 1.2×10^{-3}
c. 3.1
d. 8.5×10^{2}
e. 2.6×10^{6}

5. A sealed tube is prepared with 1.07 atm PCl_5 at 500 K. The PCl_5 decomposes until equilibrium is established; 1.54 atm is the equilibrium pressure of the tube. Calculate K_p using the equation: **$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$**

   a. 0.052
   b. 0.20
   c. 0.27
   d. 0.37
   e. 2.2

6. Hydrogen monoiodide can decompose into hydrogen and iodine gases: **$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$ $K_p = 0.016$** at -17 °C. If 0.820 atm of HI(g) is sealed in a flask at -17 °C, what is the pressure of each gas when equilibrium is established?

   a. HI = 0.576 atm, H_2 = 0.096 atm, I_2 = 0.096 atm
   b. HI = 0.654 atm, H_2 = 0.083 atm, I_2 = 0.083 atm
   c. HI = 0.728 atm, H_2 = 0.092 atm, I_2 = 0.092 atm
   d. HI = 0.737 atm, H_2 = 0.083 atm, I_2 = 0.083 atm
   e. HI = 0.768 atm, H_2 = 0.111 atm, I_2 = 0.111 atm

7. Using the chemical reactions below, determine the equilibrium constant for the following reaction:
   $Ca^{2+}(aq) + 2\ H_2O(l) \rightleftharpoons Ca(OH)_2(s) + 2\ H^+(aq)$

   $Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ OH^-(aq)$ $\quad K = 6.5 \times 10^{-6}$
   $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ $\quad K = 1.0 \times 10^{-14}$

   a. 1.5×10^{-23}
   b. 6.5×10^{-20}
   c. 1.3×10^{-19}
   d. 1.5×10^{-9}
   e. 1.5×10^{19}

8. Hydrogen and iodine react to form hydrogen monoiodide according to: **$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$ $K_c = 0.504$** at 25 °C. If initial concentrations of 0.170 M H_2 and 0.170 M I_2 are allowed to equilibrate, what is the equilibrium concentration of HI?

   a. 0.0445 M
   b. 0.0891 M
   c. 0.0684 M
   d. 0.0706 M
   e. 0.0129 M

9. Which of the following is never a Brønsted-Lowry acid in an aqueous solution?

   a. hydrogen monochloride, HCl(g)
   b. dihydrogen monosulfide, $H_2S(g)$
   c. ammonium chloride, $NH_4Cl(s)$
   d. hydrogen monofluoride, HF(g)
   e. sodium perchlorate, $NaClO_4(s)$

10. What is the conjugate base of $[Cr(H_2O)_6]^{3+}(aq)$?

   a. H_3O^+
   b. $[Cr(H_2O)_5OH]^{2+}$
   c. $[Cr(H_2O)_5H_3O]^{4+}$
   d. $[Cr(H_2O)_6]^{2+}$
   e. $[Cr(H_2O)_5]^{3+}$

11. At 25 °C, what is the H_3O^+ concentration in 0.044 M NaOH(aq)?

    a. 4.4×10^{-16} M
    b. 2.3×10^{-13} M
    c. 4.4×10^{-7} M
    d. 1.36 M
    e. 12.6 M

12. Assuming equal initial concentrations of the given species, which of the following weak acids has the strongest conjugate base in an aqueous solution?

    a. acetic acid, $K_a = 1.8 \times 10^{-5}$
    b. formic acid, $K_a = 1.8 \times 10^{-4}$
    c. hydrogen sulfite ion, $K_a = 6.2 \times 10^{-8}$
    d. nitrous acid, $K_a = 4.5 \times 10^{-4}$
    e. phosphoric acid, $K_a = 7.5 \times 10^{-3}$

13. Given the following acid dissociation constants,
    $K_a\text{ (HF)} = 7.2 \times 10^{-4}$
    $K_a\text{ (NH}_4^+\text{)} = 5.6 \times 10^{-10}$
    determine the equilibrium constant for the reaction below at 25 ºC.
    $$\mathbf{HF(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + F^-(aq)}$$

    a. 4.0×10^{-13}
    b. 1.3×10^{-8}
    c. 7.8×10^{-7}
    d. 1.3×10^{6}
    e. 2.5×10^{12}

14. What is the pH of 5.0×10^{-3} M HF? The K_a for hydrofluoric acid is 7.2×10^{-4}. *Hint: Is 100*K < C?*

    a. 2.72
    b. 2.80
    c. 4.60
    d. 5.44
    e. 6.12

15. A solution is made by diluting 0.50 mol NaClO to a volume of 3.0 L with water. What is the pH of the solution? (K_b of $ClO^{-1} = 2.9 \times 10^{-7}$)

    a. 3.66
    b. 7.46
    c. 10.34
    d. 10.58
    e. 13.22

16. What is the effect of adding 10 mL of 0.1 M NaOH(aq) to 100 mL of 0.2 M NH_4^+(aq)?

    1. The pH will decrease.
    2. The concentration of NH_3 will increase.
    3. The concentration of NH_4^+ will decrease.

    a. 1 only
    b. 2 only
    c. 3 only
    d. 2 and 3
    e. 1, 2, and 3

17. What is the pH of a solution that results from adding 25 mL of 0.50 M NaOH to 75 mL of 0.50 M CH_3CO_2H? (Note that the K_a of $CH_3CO_2H = 1.8 \times 10^{-5}$)

    a. 2.67
    b. 3.17
    c. 4.44
    d. 5.04
    e. 5.35

18. What is the pH of an aqueous solution of 0.30 M HF and 0.15 M F^-? (K_a of HF = 7.2×10^{-4})

    a. 1.83
    b. 2.84
    c. 3.14
    d. 3.44
    e. 10.86

19. Which of the following combinations would be best to buffer an aqueous solution at a pH of 2.0?

    a. H_3PO_4 and $H_2PO_4^-$, $K_{a1} = 7.5 \times 10^{-3}$
    b. HNO_2 and NO_2^{-1}, $K_a = 4.5 \times 10^{-4}$
    c. CH_3CO_2H and CH_3COO^{-1}, $K_a = 1.8 \times 10^{-5}$
    d. $H_2PO_4^{-1}$ and HPO_4^{2-}, $K_{a2} = 6.2 \times 10^{-8}$
    e. NH_4^+ and NH_3, $K_a = 5.7 \times 10^{-10}$

20. What is the pH of the buffer that results when 11 g of $NaCH_3CO_2$ is mixed with 85 mL of 1.0 M CH_3CO_2H and diluted with water to 1.0 L? (K_a of $CH_3CO_2H = 1.8 \times 10^{-5}$)

    a. 2.91
    b. 3.86
    c. 4.55
    d. 4.74
    e. 4.94

21. The K_a of hypochlorous acid, HClO, is 3.5×10^{-8}. What $[ClO^-]/[HClO]$ ratio is necessary to make a buffer with a pH of 7.71?

    a. 2.0×10^{-8}
    b. 0.25
    c. 0.56
    d. 1.8
    e. 3.9

22. What volume of 0.50 M NaOH should be added to 2.0 L of 0.25 M HCO_3^{-1} to make a buffer with a pH of 10.02? (Note that the pK_a of HCO_3^{-1} = 10.32)

    a. 0.17 mL
    b. 83 mL
    c. 2.5×10^2 mL
    d. 3.3×10^2 mL
    e. 5.0×10^2 mL

23. A volume of 25.0 mL of 0.100 M HCO_2H(aq) is titrated with 0.100 M NaOH(aq). What is the pH after the addition of 12.5 mL of NaOH? (K_a for $HCO_2H = 1.8 \times 10^{-4}$)

    a. 2.52
    b. 3.74
    c. 4.74
    d. 7.00
    e. 10.26

24. A 50.0 mL sample of 0.0240 M NH_3(aq) is titrated with aqueous hydrochloric acid. What is the pH after the addition of 15.0 mL of 0.0600 M HCl(aq)? (K_b of $NH_3 = 1.8 \times 10^{-5}$)

    a. 8.78
    b. 8.86
    c. 9.25
    d. 9.38
    e. 9.73

25. Which is the best colored indicator to use in the titration of 0.0010 M $CH_3CO_2^{-1}$(aq) with HCl(aq)? Why? (Note that the K_b of $CH_3CO_2^{-1} = 5.6 \times 10^{-10}$)

Indicator	pK_a
Bromocresol green	4.7
Phenol Red	7.8
Phenolphthalein	9.0

    a. Bromocresol green. The pH at the equivalence point is less than 7.0.
    b. Phenol Red. The pK_b of acetate ion and the pK_b of the indicator are similar.
    c. Phenol Red. The equivalence point of an acid-base titration occurs at a pH of 7.0.
    d. Phenolphthalein. The pK_b of acetate ion and the pK_b of the indicator are similar.
    e. Phenolphthalein. The pH at the equivalence point is greater than 7.0.

Part II: Short Answer / Calculation. *Show all work!*

1. Consider a 1.00 L solution which is 0.700 M CH_3CO_2H and 0.600 M $NaCH_3CO_2$. $K_a = 1.8*10^{-5}$

   a. What is the pH of the initial solution?

   b. Calculate the pH upon adding 10.00 mL of 1.00 M HCl to the solution from part a.

   c. Calculate the pH upon adding 15.00 mL of 2.10 M NaOH to the solution from part a.

2. Consider the reaction: $\mathbf{B_2H_6(g) \rightleftharpoons 2\ BH_3(g), \Delta H = +112\ kJ}$ Use Le Chatelier's principle to predict the effect of the following changes on this reaction at equilibrium. Write **RIGHT**, **LEFT** or **NO CHANGE** to indicate the effect observed.

	Effect
Addition of B_2H_6:	_____________
Addition of a catalyst:	_____________
Increasing the pressure:	_____________
Removal of BH_3:	_____________
Increasing temperature:	_____________

3. A solution contains 50.0 mL of 0.100 M acetic acid (CH_3CO_2H). $K_a = 1.8*10^{-5}$

   a. What is the pH of the initial acetic acid solution?

   b. What is the pH after 10.0 mL of 0.100 M NaOH has been added to the mixture?

   c. What is the pH after 40.0 mL of 0.100 M NaOH has been added to the mixture?

   d. How many mL of 0.100 M NaOH are required to reach the equivalence point?

   e. How many mL of 0.100 M NaOH are required to reach the half-equivalence point? What is the pH of the solution at the half-equivalence point?

   f. What is the pH at the equivalence point?

   g. What is the pH after 60.0 mL of 0.100 M NaOH has been added to the mixture?

CH 223 Sample Exam
Exam I Name: ____ Lab Section: ______
Answers

Part I: Multiple Choice Questions

1. A
2. B
3. B
4. B

5. D
6. B
7. A
8. B
9. E
10. B

11. B
12. C
13. D
14. B
15. C

16. D
17. C
18. B
19. A
20. E
21. D

22. D
23. B
24. A
25. A

Part II: Short Answer / Calculation.

1. Buffer question:
    a. 4.67
    b. 4.66
    c. 4.72
2. Le Chatelier's Principle question:
    a. right
    b. no change
    c. left
    d. right
    e. right
3. Titration question:
    a. 2.87
    b. 4.14
    c. 5.34
    d. 50.0 mL
    e. 25.0 mL, 4.74
    f. 8.72
    g. 11.96

CH 223 Sample Exam
Exam II Name: ____ Lab Section: ______

Part I: Multiple Choice Questions (100 Points) There is *only* one best answer for each question.

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1. Which of the following equations is the solubility product for magnesium iodate, $Mg(IO_3)_2$?

   a. $K_{sp} = [Mg^{2+}][I^{-1}]^2[O^{-2}]^6$
   b. $K_{sp} = [Mg^{2+}][I^{-1}]^2[3O^{-2}]^2$
   c. $K_{sp} = [Mg^{2+}][IO_3^{-1}]$
   d. $K_{sp} = [Mg^{2+}]^2[IO_3^{-1}]$
   e. $K_{sp} = [Mg^{2+}][IO_3^{-1}]^2$

2. The solubility of $SrSO_4$ in water is 0.107 g in 1.0 L at 25 °C. What is the value of K_{sp} for $SrSO_4$?

   a. 3.4×10^{-7}
   b. 5.8×10^{-4}
   c. 1.2×10^{-3}
   d. 1.1×10^{-2}
   e. 2.1×10^{-1}

3. The solubility of lead (II) chloride, $PbCl_2$, is $1.6 \text{ x } 10^{-2}$ M. What is the K_{sp} of $PbCl_2$?

   a. $5.0 \text{ x } 10^{-4}$
   b. $4.1 \text{ x } 10^{-6}$
   c. $3.1 \text{ x } 10^{-7}$
   d. $1.6 \text{ x } 10^{-5}$
   e. $1.6 \text{ x } 10^{-2}$

4. Calculate the maximum concentration (in M) of silver ions (Ag^+) in a solution that contains 0.025 M of CO_3^{2-}. The K_{sp} of Ag_2CO_3 is $8.1 \text{ x } 10^{-12}$.

   a. $1.8 \text{ x } 10^{-5}$
   b. $1.4 \text{ x } 10^{-6}$
   c. $2.8 \text{ x } 10^{-6}$
   d. $3.2 \text{ x } 10^{-10}$
   e. $8.1 \text{ x } 10^{-12}$

5. The K_{sp} for $Zn(OH)_2$ is $5.0 \text{ x } 10^{-17}$. Determine the molar solubility of $Zn(OH)_2$ in a buffer solution with a pH of 11.5.

   a. $5.0 \text{ x } 10^{6}$
   b. $1.2 \text{ x } 10^{-12}$
   c. $1.6 \text{ x } 10^{-14}$
   d. $5.0 \text{ x } 10^{-12}$
   e. $5.0 \text{ x } 10^{-17}$

6. The molar solubility of __________ is not affected by the pH of the solution.

   a. Na_3PO_4
   b. NaF
   c. KNO_3
   d. $AlCl_3$
   e. MnS

7. Consider the reaction

$Zn(OH)_2(s) + 2\ OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$ $\quad \mathbf{K = 8.7 \times 10^{-2}}$

If K_{sp} for $Zn(OH)_2$ is $\mathbf{3.0 \times 10^{-17}}$, what is the value of the formation constant, K_{form}, for the reaction below?

$\mathbf{Zn^{2+}(aq) + 4\ OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)}$

a. 2.6×10^{-18}
b. 3.4×10^{-16}
c. 2.9×10^{15}
d. 3.3×10^{16}
e. 3.8×10^{17}

8. The following anions can be separated by precipitation as silver salts: Cl^{-1}, Br^{-1}, I^{-1}, CrO_4^{2-}. If Ag^+ is added to a solution containing the four anions, each at a concentration of 0.10 M, in what order will they precipitate?

Compound	K_{sp}
AgCl	1.8×10^{-10}
Ag_2CrO_4	1.1×10^{-12}
AgBr	5.4×10^{-13}
AgI	8.5×10^{-17}

a. $AgCl \rightarrow Ag_2CrO_4 \rightarrow AgBr \rightarrow AgI$
b. $AgI \rightarrow AgBr \rightarrow Ag_2CrO_4 \rightarrow AgCl$
c. $Ag_2CrO_4 \rightarrow AgCl \rightarrow AgBr \rightarrow AgI$
d. $Ag_2CrO_4 \rightarrow AgI \rightarrow AgBr \rightarrow AgCl$
e. $AgI \rightarrow AgBr \rightarrow AgCl \rightarrow Ag_2CrO_4$

9. A statement of the second law of thermodynamics is that

a. spontaneous reactions are always exothermic.
b. energy is conserved in a chemical reaction.
c. the Gibbs free energy is a function of both enthalpy and entropy.
d. $\Delta S = -\Delta H$ for any chemical reaction.
e. in a spontaneous process, the entropy of the universe increases.

10. As defined by Ludwig Boltzmann, the third law of thermodynamics states that

a. in a spontaneous process, the entropy of the universe increases.
b. there is no disorder in a perfect crystal at 0 K.
c. the total entropy of the universe is always increasing.
d. the total energy of the universe is constant.
e. mass and energy are conserved in all chemical reactions.

11. Which of the following processes involves a decrease in entropy?

a. the decomposition of $NH_3(g)$ into $H_2(g)$ and $N_2(g)$ gas
b. the dissolution of NaCl in water
c. the condensation of steam to liquid water
d. the evaporation of ethanol
e. the sublimation of dry ice (i.e., $CO_2(s)$)

12. Calculate the standard entropy change for the following reaction,

$$2\ HgO(s) \rightleftharpoons 2\ Hg(l) + O_2(g)$$

given $S°[HgO] = 70.3$ J/K·mol, $S°[Hg(l)] = 76.0$ J/K·mol, and $S°[O_2(g)] = 205.1$ J/K·mol.

a. -216.5 J/K
b. +210.8 J/K
c. +216.5 J/K
d. +351.4 J/K
e. +497.7 J/K

13. Predict the signs of ΔH, ΔS, and ΔG for the evaporation of water 25 °C.

a. $\Delta H > 0, \Delta S < 0, \Delta G < 0$
b. $\Delta H > 0, \Delta S > 0, \Delta G > 0$
c. $\Delta H < 0, \Delta S > 0, \Delta G < 0$
d. $\Delta H < 0, \Delta S > 0, \Delta G > 0$
e. $\Delta H < 0, \Delta S < 0, \Delta G < 0$

14. The dissolution of ammonium nitrate occurs spontaneously in water at 25 °C. As NH_4NO_3 dissolves, the temperature of the water decreases. What are the signs of ΔH, ΔS, and ΔG for this process?

a. $\Delta H > 0, \Delta S < 0, \Delta G > 0$
b. $\Delta H > 0, \Delta S > 0, \Delta G > 0$
c. $\Delta H > 0, \Delta S > 0, \Delta G < 0$
d. $\Delta H < 0, \Delta S < 0, \Delta G < 0$
e. $\Delta H < 0, \Delta S > 0, \Delta G > 0$

15. Diluting concentrated sulfuric acid with water can be dangerous. The temperature of the solution can increase rapidly. What are the signs of ΔH, ΔS, and ΔG for this process?

a. $\Delta H < 0, \Delta S > 0, \Delta G < 0$
b. $\Delta H < 0, \Delta S < 0, \Delta G < 0$
c. $\Delta H < 0, \Delta S > 0, \Delta G > 0$
d. $\Delta H > 0, \Delta S > 0, \Delta G < 0$
e. $\Delta H > 0, \Delta S < 0, \Delta G > 0$

16. At what temperatures will a reaction be spontaneous if ΔH = -76.0 kJ and ΔS = +231 J/K?

a. All temperatures below 329 K
b. Temperatures between 0 K and 231 K
c. All temperatures above 329 K
d. The reaction will be spontaneous at any temperature.
e. The reaction will never be spontaneous.

17. Calculate $\Delta G°_{rxn}$ for the reaction below at 25.0 °C

$$CO(g) + H_2O(l) \rightarrow H_2(g) + CO_2(g)$$

given $\Delta G°_f[CO(g)] = -137.2$ kJ/mol, $\Delta G°_f[H_2O(l)] = -237.2$ kJ/mol and $\Delta G°_f[CO_2(g)] = -394.4$ kJ/mol.

a. -768.8 kJ
b. -294.4 kJ
c. -20.0 kJ
d. +20.0 kJ
e. +768.8 kJ

18. __________ is reduced in the following reaction: $\mathbf{Cr_2O_7^{2-} + 6\ S_2O_3^{2-} + 14\ H^{+1} \rightarrow 2\ Cr^{3+} + 3\ S_4O_6^{2-} + 7\ H_2O}$

    a. Cr^{6+}
    b. S^{2+}
    c. H^{+1}
    d. O^{2-}
    e. $S_4O_6^{2-}$

19. Which substance is the reducing agent in the following reaction: $\mathbf{Cr_2O_7^{2-} + 3\ Ni + 14\ H^{+1} \rightarrow 2\ Cr^{3+} + 3\ Ni^{2+} + 7\ H_2O}$

    a. Ni
    b. H^{+1}
    c. $Cr_2O_7^{2-}$
    d. H_2O
    e. Ni^{2+}

20. The balanced half-reaction in which one mole of chlorine gas is reduced to the aqueous chloride ion is a __________ process.

    a. one-electron
    b. two-electron
    c. four-electron
    d. three-electron
    e. six-electron

21. The half-reaction occurring at the ***anode*** in the balanced reaction shown below is __________.

    $$\mathbf{3\ MnO_4^{1-}(aq) + 5\ Fe(s) + 24\ H^{+1}(aq) \rightarrow 3\ Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 12\ H_2O(l)}$$

    a. $MnO_4^{1-}(aq) + 8\ H^{+1}(aq) + 5\ e^{-1} \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$
    b. $2\ MnO_4^{1-}(aq) + 12\ H^{+1}(aq) + 6\ e^{-1} \rightarrow 2\ Mn^{2+}(aq) + 3\ H_2O(l)$
    c. $Fe(s) \rightarrow Fe^{3+}(aq) + 3\ e^{-1}$
    d. $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^{-1}$
    e. $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-1}$

22. The standard cell potential ($E°_{cell}$) of the reaction below is **+0.126 V**. The value of **ΔG°** for the reaction is __________ kJ/mol.

    $$\mathbf{Pb(s) + 2\ H^{+1}(aq) \rightarrow Pb^{2+}(aq) + H_2(g)}$$

    a. -24.3
    b. +24.3
    c. -12.6
    d. +12.6
    e. -50.8

23. How many grams of Ca metal are produced by the electrolysis of molten $CaBr_2$ using a current of 30.0 amp for 10.0 hours?

    a. 22.4
    b. 448
    c. 0.0622
    d. 224
    e. 112

24. Which one of the following reactions is a redox reaction?

    a. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
    b. $Pb^{2+}(aq) + 2\ Cl^{-1}(aq) \rightarrow PbCl_2(aq)$
    c. $AgNO_3(aq) + HCl(aq) \rightarrow HNO_3(aq) + AgCl(s)$
    d. None of the above is a redox reaction.
    e. All of the above are redox reactions

25. What is the coefficient for Fe^{3+} when the following equation is ***balanced***? $CN^{-1} + Fe^{3+} \rightarrow CNO^{-1} + Fe^{2+}$, pH = 10.75

    a. 1
    b. 2
    c. 3
    d. 4
    e. 5

<u>Part II</u>: Short Answer / Calculation. *Show all work!*

1. A solution contains 0.10 M Cl^- and 0.10 M Br^- ions. K_{sp} for AgCl = 1.8×10^{-10}, K_{sp} for AgBr = 3.3×10^{-13}. (10 points)
    a. $AgNO_3$ is added until a white solid just begins to precipitate. What is the identity of the precipitate?
    b. What is the concentration of the less soluble ion once the more soluble ion begins to precipitate out of solution?

Part II: Short Answer / Calculation *(continued) Show all work!*

2. Calculate $\Delta G°$ for the reaction below at 25.0 °C. (10 points)

$$P_4(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(l)$$

Species	$\Delta H°_f$ (kJ/mol)	$S°_f$ (J/K·mol)
$P_4(s)$	0	22.80
$H_2O(l)$	-285.8	69.95
$H_3PO_4(l)$	-1279.0	110.5

3. Calculate $\Delta G°$ and the equilibrium constant, K_{eq}, for the disproportionation reaction (below) of Cu^{+1} at 25 °C:

$$2\ Cu^{+1}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

given the following thermodynamic information. (10 points)

$Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$ $E° = +0.518$ V

$Cu^{2+}(aq) + 2\ e^{-} \rightarrow Cu(s)$ $E° = +0.337$ V

CH 223 Sample Exam
Exam II Name: ____ Lab Section: ______
Answers

Part I: Multiple Choice Questions

1. E
2. A
3. D
4. A
5. D
6. C

7. C
8. E
9. E
10. B
11. C

12. C
13. B
14. C
15. A
16. D
17. C

18. A
19. A
20. B
21. C
22. A
23. D

24. D
25. B

Part II: Short Answer / Calculation.

1. Precipitation question:
    a. AgBr
    b. 1.8×10^{-4} M
2. $\Delta G = -3401$ kJ
3. $\Delta G = -34.9$ kJ, $K = 1.3 \times 10^{6}$