**Instructor:** David Glueck  (305 Burke)  6-1568  
**Office Hours:** Monday 1-3; Wednesday, 2-3, or by appointment.


**Lectures:** M,W,F 8:45–9:50 AM, 007 Steele.  
**X-hour:** Th 9:00–9:50 AM, 007 Steele:  **We will use this period frequently.**
30 lectures are scheduled (see below).

**Laboratory:** Th/Fr 2-6 PM, 306 Steele.  NOTE -- graduate students do not need to do the lab experiments, but they are responsible for this material on the exams.  There will be a mandatory lab lecture on 1/12 in the x-hour slot.  Labs will begin Thursday 1/12.

**WEB:** [www.dartmouth.edu/~chem64/](http://www.dartmouth.edu/~chem64/).  Some of the course material will be at this site.

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### APPROXIMATE LECTURE SCHEDULE

<table>
<thead>
<tr>
<th>Week</th>
<th>Dates</th>
<th>Topics</th>
<th>Chapter/Sections</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/4, 1/5,* 1/6</td>
<td>Overview; Molecular Structure, Symmetry, Point Groups</td>
<td>3.1-3.3, 4.1-4.4</td>
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<tr>
<td>2</td>
<td>1/9,1/11,1/12,*1/13</td>
<td>Character Tables, Vibrational Spectroscopy</td>
<td>4.5-4.6, 4.8-4.9</td>
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<tr>
<td></td>
<td><em><em>1-12</em> = LAB LECTURE. YOU MUST ATTEND</em>*</td>
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<tr>
<td>3†</td>
<td>1/18, 1/19,*1/20</td>
<td>Orbital Symmetry, MO Theory of Diatomics, MO Theory of Polyatomics, Walsh Diagrams</td>
<td>1.3-1.8, 4.7, 3.4-3.13</td>
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<td></td>
<td><strong>EXAM #1: TUESDAY, JANUARY 24, 7:30–9:30 PM Wilder 104</strong></td>
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<tr>
<td>4</td>
<td>1/23, 1/25, 1/27</td>
<td>Lewis Acids &amp; Bases, Hardness &amp; Softness</td>
<td>5 (esp. 5.1-5.3, 5.7-5.14)</td>
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<tr>
<td>5</td>
<td>1/30, 2/1, 2/3</td>
<td>Transition Metal Coordination Chemistry Structures, Isomers &amp; Nomenclature</td>
<td>7.1–7.3</td>
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<tr>
<td>6† †</td>
<td>2/6, 2/8, 2/9*</td>
<td>Ligand Field Theory, Magnetism, MO Theory</td>
<td>7.4–7.7</td>
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<tr>
<td>7</td>
<td>2/13, 2/15, 2/17</td>
<td>Electronic Spectra of Transition Metal Complexes</td>
<td>13.1–13.5</td>
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<td><strong>EXAM #2: TUESDAY, FEBRUARY 21, 7:30–9:30 PM Wilder 104</strong></td>
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<td>8</td>
<td>2/20, 2/22, 2/24</td>
<td>Ligand Substitution, Mechanisms of Electron Transfer Reactions</td>
<td>7.8, 14.1–14.10</td>
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<td></td>
<td>14.12-14.13</td>
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<tr>
<td>10</td>
<td>3/6, 3/8</td>
<td>Organometallic Chemistry</td>
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</tr>
</tbody>
</table>

**FINAL EXAM (Monday, March 13, 11:30 AM)**  
**Location TBA**

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* Planned X-Hour Class.  Other X-Hour Classes may be held.  
† No class held on Monday, January 17, Martin Luther King Day.  
†† No class on Winter Carnival Holiday Friday, Feb. 10; no lab this week.
Grading Point Distributions:

<p>| | |</p>
<table>
<thead>
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<tbody>
<tr>
<td>Laboratory</td>
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<td>Exams 1</td>
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<td>2</td>
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<tr>
<td>Final Exam</td>
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<tr>
<td><strong>TOTAL</strong></td>
<td><strong>400</strong></td>
</tr>
</tbody>
</table>

Failing the laboratory will automatically result in failure of the entire course.

Students with Disabilities: I encourage students with disabilities, including "invisible" disabilities like chronic diseases and learning disabilities, to discuss with me after class or during office hours any appropriate accommodations which might be helpful to them.

HONOR PRINCIPLE: It is important to be explicit in stating how the broad principle of academic honor applies in this course. Please feel free to inquire further if the statements below are not adequate.

1. Examinations. Any of the numerous activities normally considered cheating are violations. Examinations are not proctored; however, it will probably be necessary for me to be present from time to time during the exam to answer questions which arise.

Since the exam graders do not claim to have perfect records of accuracy, claims of injustice in grading will be carefully considered. The changing of an answer followed by the return of the paper to the instructor for reconsideration is a direct violation of the Honor Principle.

2. Laboratory. The principle of academic honor is at the very heart of experimental science. The following remarks apply to the laboratory work in Chemistry 64:

   Unless permission is granted by the instructor, use of another student's laboratory data is a violation. When use of another's data is allowed, the source of the data must be indicated. Fabrication of data or alteration of your own data to secure some desired result is also a violation. In the case of experiments where two students work together and data have been recorded in one student's notebook, a copy of the data may be made in the other student's notebook with an appropriate citation to the location of the original data. Any other material in the notebook which has been copied from any source whatever must also be provided with a source citation. The laboratory report must represent your independent calculations and individual conclusions although comparison of numerical results with another student is permitted. Of course, direct copying of any portion of another student's laboratory report is a clear violation of the Honor Principle.

3. Problem Assignments. Homework is excluded from Honor Principle constraints. However, students are strongly encouraged to tackle each problem set independently until the point is reached where further time and effort seem futile. At that point, collaboration with one's fellow students is encouraged.

MOLECULAR MODELS: You will need a set of molecular models containing atoms with coordination number greater than 4. Buy them at the bookstore, or online at http://vig.prenhall.com:8081/catalog/academic/product/0,1144,0139554440-FEA,00.html. Be sure to get them before the first lab (1/12 or 1/13)!

LABORATORY MANUAL: Separate handout. Lab notebooks will be provided. Lab lecture 1/12; first lab is Thursday 1/12 or Friday 1/13.

LABORATORY: The laboratory portion of this course will introduce you to techniques and spectroscopic methods employed by Inorganic Chemists to synthesize and characterize molecules. Of course many of these techniques and methods can also be applied to the synthesis and characterization of organic molecules.

FURTHER DETAILS ON THE LAB PORTION OF THIS COURSE ARE PROVIDED ON A SEPARATE HANDBOUT
ADVERTISEMENT

MORE INORGANIC CHEMISTRY!

Want to see more inorganic chemistry, with applications?

Take some or all of these cross-listed undergraduate/graduate classes, offered in the spring and fall terms:

CHEM 90/130: Organometallic Chemistry (Spring 2007, Hughes)
CHEM 91/131: Catalysis (Fall 2007, Glueck)
CHEM 92/132: Bio-Inorganic Chemistry (Spring 2006, Wilcox)

• Small class sizes (5 in Chem 91/131 fall 2005)
• No lab.
Chem 64 Reserve Reading List

Note: For almost all of this course, you will not need to look at any of these books (besides the textbook and the solutions manual.) Some may be helpful in giving a different viewpoint or more details. The encyclopedic Cotton+Wilkinson text is usually a good place to start, and is often useful for the lab.

http://libcat.dartmouth.edu/search/rchem/rchem/1%2C5%2C5%2CB/frameset&FF=rchem+064+w05&1%2C2C1%2C2C

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<th>Title</th>
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<tr>
<td>Cotton &amp; Wilkinson</td>
<td>Advanced Inorganic Chemistry 6th</td>
<td>1</td>
<td>QD 151.2 .C68 1999</td>
</tr>
<tr>
<td>Cotton, Wilkinson &amp; Gaus</td>
<td>Basic Inorganic Chemistry 6th</td>
<td>1</td>
<td>QD 151.2 .C69 1999</td>
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<tr>
<td>Huheey</td>
<td>Inorganic Chemistry</td>
<td>1</td>
<td>QD 151.2 .H84 1983</td>
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<td>Purcell &amp; Kotz</td>
<td>Inorganic Chemistry</td>
<td>1</td>
<td>QD 151.2 .P87</td>
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<tr>
<td>Cotton</td>
<td>Concepts &amp; Models of Inorganic Chem. 3rd</td>
<td>1</td>
<td>QD 475 .D65 1999</td>
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<td>Vincent</td>
<td>Molecular Symmetry &amp; Group Theory</td>
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<td>QD 461 .C65 1990</td>
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<td>Symmetry &amp; Structure 2nd</td>
<td>1</td>
<td>QD 471 .K47516 1995</td>
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<td>Karplus &amp; Porter</td>
<td>Atoms &amp; Molecules</td>
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<td>QD 461 .K33</td>
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<td>Ballhausen &amp; Gray</td>
<td>Molecular Orbital Theory</td>
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<td>QD 461 .B24</td>
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<tr>
<td>Ballhausen</td>
<td>Introduction to Ligand Field Theory</td>
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<td>QD471 .B3</td>
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<td>Figgis</td>
<td>Introduction to Ligand Fields</td>
<td>1</td>
<td>QD 475 .F57</td>
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<td>Drago</td>
<td>Physical Methods for Chemists 2nd</td>
<td>1</td>
<td>QD 453.2 .D7 1992</td>
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<tr>
<td>Nakamoto</td>
<td>Infrared and Raman Spectra of Inorganic and Coordination Compounds 5th</td>
<td>1</td>
<td>QD 96 .I5N33 1997 v.1, v.2</td>
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<tr>
<td>Langford &amp; Gray</td>
<td>Ligand Substitution Processes</td>
<td>1</td>
<td>QD 471 .L23</td>
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<tr>
<td>Wilkins</td>
<td>The Study of Kinetics &amp; Mechanisms</td>
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<td>QD 474 .W54</td>
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<td>Wilkins</td>
<td>Reactions of Transition Metal Complexes</td>
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<td>QD 471 .L23</td>
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<td>Angelici</td>
<td>Synthesis &amp; Techniques in Inorganic Chemistry 2nd</td>
<td>1</td>
<td>QD 155 .A53 1977</td>
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<tr>
<td>Jolly</td>
<td>The Synthesis &amp; Characterization of Inorganic Compounds</td>
<td>1</td>
<td>QD 156 .J65</td>
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<tr>
<td>Shriver, Atkins</td>
<td>Inorganic Chemistry, 3rd Edn.</td>
<td>1</td>
<td></td>
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<tr>
<td>Strauss</td>
<td>Solutions to Inorg. Chem.</td>
<td>1</td>
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</tbody>
</table>
GENERAL INFORMATION

Instructor: David Glueck (305 Burke)

Teaching Assistants: Brian Anderson (318 Burke)
Jian Yuan (310 Burke)

Time: Thursday or Friday, 2:00-6:00 PM, 306 Steele

Laboratory Notebook: this will be issued when you check into the lab (do not purchase one at the bookstore).

Schedule: Your lab manual contains six experiments (see the brief descriptions on the next page). Each laboratory period will begin with some comments in the laboratory about the experiment; please do not be late for the start of lab. Experiment 1 is a "dry lab" and will require no lab report.

Lab reports for the remaining experiments will be due within one week of your lab section. (Thus, if you have lab on Thursday January 17, your report is due on Thursday January 24). You can turn in reports to the TA's or to me. Please don't pester the TA's with questions about the lab reports; ask me instead.

There will be a penalty for late laboratory reports!

- one or two days late -- 20% penalty. Example: you're 2 days late and get a score of 8 out of 10. After deducting 20% your corrected score is 6.4 out of 10.
- 3 to 6 days late -- 40% penalty. Example: you're 5 days late and get a score of 6 out of 10. After deducting 40% your corrected score is 3.6 out of 10.
- more than 6 days late -- 60% penalty. Example, you're 2 weeks late and get a score of 4 out of 10. After deducting 60% your corrected score is 1.6 out of 10.

Because of possible delays between doing the experiment and writing up the lab report, accurate and complete observations in your notebook are crucial. This is especially important since part of your lab grade (see below) will be based on evaluation of your notebook.

Fees: The standard laboratory charge, which includes the cost of nonreturnable items and the laboratory notebook, is $16.00. Further, additional charges will be made for breakage, and/or excessive damage and the total sum will be added to your College bill at the end of the term. Please take good care of your equipment--it is expensive.
Grading: Your lab grade is based on:

- Reports: 70%
- Notebooks: 20%
- Instructor's Evaluation of Technique and Comprehension: 10%

The laboratory portion of the course will count for about 25% of the final grade. However, failure to complete the laboratory (this includes turning in the lab reports!) will result in a failing grade.
LABORATORY EXPERIMENTS

1. **Molecular Structure and Symmetry (1/12 - 1/13):** Apply VSEPR to build models of molecules and assign them to their molecular symmetry groups (point groups).

2. **Spectra and Structure of Nitrile Complexes (1/19 - 1/20):** Prepare a copper acetonitrile complex and a palladium benzonitrile complex. Use IR and NMR spectra to determine their structures.

3. **Synthesis and Resolution of a Chiral Nickel Complex (1/26 - 1/27):** Prepare and separate a racemic mixture of Ni-phenanthroline complexes. Study the chiroptical properties of one enantiomer of the Ni complex.

4. **Four-Coordinate Nickel Diphosphine Complexes (2/2 - 2/3):** Prepare two closely related diphosphine complexes of nickel dichloride, and compare their physical and spectroscopic properties.

   5. **No lab this week, Winter Carnival holiday Friday 2/10!**

6. **Stabilization of Chromium(II) by Complexation (2/16 - 2/17):** Use inert atmosphere techniques to prepare air sensitive solutions of Cr(II). Stabilize this oxidation state by ligand coordination and make a compound with a metal-metal multiple bond.

7. **Preparation of Chromium(III) Compounds: the Spectrochemical Series (2/23 - 2/24):** Prepare Cr(III) compounds by three different procedures, in one case using liquid ammonia, and study their electronic properties that lead to their distinctive colors spectroscopically.
ACADEMIC HONOR PRINCIPLE

The principle of academic honesty is at the very heart of experimental science. The following remarks apply to the laboratory work in Chemistry 64:

· Unless permission is granted by the instructor, use of another student's laboratory data is a violation.

· When use of another’s data is allowed, the source of the data must be indicated.

· Fabrication of data or alteration of your own data to secure some desired result is also a violation. [This happened in Winter 2001 and resulted in a 1-term suspension.]

· In the case of experiments where two students work together and data have been recorded in one student's notebook, a copy of the data may be made in the other student's notebook with an appropriate citation to the location of the original data. Any other material in the notebook which has been copied from any source whatever must also be provided with a source citation.

· The laboratory report must represent your independent calculations and individual conclusions, although comparison of numerical results with another student is permitted, with appropriate attribution.

· Of course, direct copying of any portion of another student's laboratory report is a clear violation of the Honor Principle.

Any violation of the Honor Principle in this course will result in notification of the College Committee on Standards.

If you have ANY QUESTIONS about how the Honor Principle applies to any situation in this course, PLEASE DO NOT HESITATE TO CONTACT YOUR INSTRUCTOR.
LABORATORY SAFETY

1. Wear safety goggles in the lab. Repeated violation of this rule will lead to ejection from the lab.

2. Never use an open flame in the lab.

3. Smoking, eating, and drinking is absolutely forbidden in this laboratory.

4. Never bring coats or bulky flammable items into the laboratory.

5. Know the location of the nearest fire extinguisher, safety shower, eye wash fountain, and exit.

6. Do all pipetting with a suction bulb. Mouth pipetting is absolutely forbidden.

7. When a reaction is left alone for extended periods of time (>1/2 hour), leave a note next to it indicating important facts for persons working in that vicinity.

8. Know the physical, chemical, physiological properties (as far as possible) of the reactants, products, and solvents used in each preparation. Be ready for questions about the toxicity of the materials which you will be using.

9. Do all manipulations in the hood unless directed otherwise.

10. Know and follow the proper disposal method for chemicals.

11. Clean up your work area in the laboratory before you leave.

12. Wash your hands thoroughly before leaving the lab.

13. If you have any questions or doubts about the experimental procedures, contact the instructor or the teaching assistants before beginning experimental work.
LABORATORY GUIDELINES

1. Safety glasses must be worn by everyone who enters the lab.

2. No sandals or shorts are to be worn while in the lab.

3. Do the experiments in the hood.

4. Cleanliness of the laboratory is the responsibility of the students who use it and the Teaching Assistants who supervise them.

   At the conclusion of each lab session:
   - All glassware must be cleaned and put in the lockers. Do not put dirty glassware in the lockers.
   - Benchtops are to be cleaned of any spills and chemical residue.
   - Balances and the areas around them are to be free of spilled chemicals and used weighing paper.
   - Reagent dispensing areas are to be free of spilled chemicals or liquid reagents.
   - Hoods are to be clean and emptied of all glassware and chemicals.

The TAs will inspect your lab station and associated common equipment areas before signing your lab notebook. They will also provide brief qualitative assessment of your notebook and lab technique each week.

6. Place all broken glassware in the SHARPS containers. Do not put broken glass in the trash.

7. Dispose of waste chemicals in the containers provided. Do not put waste chemicals or products in the lockers.

LABORATORY REPORTS

In the laboratory, record all pertinent observations and data for each experiment in a neat, concise fashion in pen in your notebook as you do the experiment. Writing up a prelab as done in other courses is also useful. Notebooks may be collected, and examined, without notice, at various times during the term; evaluation of your notebook counts as part of your lab grade.

Here is the format for the lab reports, which should be BRIEF but clearly written.

1. TITLE & DATE: The title of the experiment and the date it was done should be listed on the front page along with the name(s) of your lab partners.

2. INTRODUCTION: (BRIEF!) Background material explaining why you are performing the experiment. Information for this section can be found in the lab handout and/or in the references given at the beginning of each experiment.

3. RESULTS & DISCUSSION: What happened and how you interpret it. Information to include here: what compounds you made, their spectral data, answers to the questions from the lab manual, and discussion of the results. If you use an idea from a reference to help you answer a question, the reference should be footnoted (include the references as endnotes at the end of the report).

4. EXPERIMENTAL: Each new complex isolated should be listed separately. A good format is:

   Complex aa: A sample of $$[X \text{ g, } Y \text{ mol}]$$ was dissolved in H$_2$O (30 mL) to afford a green solution which was then added to a blue solution of $$[X \text{ g, } Y \text{ mol}]$$ in MeOH (10 mL). The solution was stirred at room temperature for one hour. Filtration of the resulting purple precipitate and subsequent washing with H$_2$O (3 x 15 mL) yielded, before recrystallization, purple crystals of $$@[X \text{ g, } Y \text{ mol, } \% \text{ yield}], \text{ m.p. } 102-104 \degree \text{C}.$$.

5. CONCLUSION: This can be brief, but you need to summarize the results.

6. REFERENCES: Use the standard American Chemical Society format:


   All lab reports MUST be printed or typed (handwritten reports will not be accepted). Spectra should be stapled to the last page or pasted into the report itself.
Just as you need to know the alphabet in order to spell words in the English language, I also expect you to know from memory the names and symbols of the first 86 elements of the Periodic Table. These are the component parts from which almost all known materials are made. The Periodic Table is your guide to the chemistry of the elements and their compounds. You should know your way around it, and be able to calculate quickly the valence electron configuration of any element in any oxidation state.

I will expect you to be familiar with the following terms, concepts and topics from your General Chemistry and Organic Chemistry courses. Some of these topics are reviewed in your text, primarily in Chapters 1 and 2, and in some class handouts. You may need to go back to your General Chemistry text to freshen up on other subjects.

IF YOU HAVE ANY PROBLEMS WITH THIS MATERIAL, COME AND ASK FOR HELP!!

A. General Chemistry (Chem 3/5 and Chem 6, or Chem 10)

Atomic orbitals: s, p, d
mathematical description and spatial visualization
(you should be able to draw them correctly from various perspectives)
angular portion (shape) & radial portion (size and penetration)
core and valence orbitals
change of phase of wavefunction in different orbital lobes - nodal characteristics
energies in hydrogen atom and in multielectron atoms and ions

Periodic table and periodic trends
electronic configuration, Aufbau Principle, Hund's Rule
symbols and names of the elements
main group, transition metals, lanthanides, actinides
ionization potential and electron affinity - electronegativity
polarizability

Thermodynamics
enthalpy (H); enthalpy-driven reaction
entropy (S); entropy-driven reaction
free energy (G) and its relation to H and S
equilibrium constant (K) and its relation to ΔG°
redox potential (E°) and its relation to ΔG°

Kinetics
rate expressions for 1st and 2nd order reactions - mechanistic implications
activation energy; Arrhenius equation, rate determining step
catalysis, effect of catalyst on equilibrium constants and rate constants
reaction coordinate; free energy reaction profile
Valence Electron Bonding Theory (coordinate covalent 2-e⁻ bonds)
- octet rule, and exceptions to it
- Valence Shell Electron Pair Repulsion Theory (VSEPR)
- hybridization - hybrid atomic orbitals
- resonance forms - evaluation of their relative importance
- isoelectronic atoms ions and molecules
- Lewis Base (e⁻ pair donor) and Acid (e⁻ pair acceptor)
- bond lengths and bond strengths
- bond polarity - molecular dipoles

Molecular Orbital Theory
- homonuclear diatomic M.O. energy level diagrams
- bonding, nonbonding, and antibonding molecular orbitals
- calculation of bond order
- σ-bonds - nodal characteristics
- π-bonds - nodal characteristics
- δ-bonds - nodal characteristics [new; to be introduced soon]

B. Organic Chemistry (Chem 51-52, or 57-58)

- nomenclature
- nucleophile (Lewis Base); S_N¹ and S_N² mechanisms
- electrophile (Lewis Acid)
- IR spectroscopy
  - identification of functional groups
  - transitions between vibrational states
- UV spectroscopy
  - transitions of electrons from ground state to excited electronic states
- Mass Spectrometry
  - parent (molecular) ion; fragmentation patterns
- Nuclear Magnetic Resonance Spectrometry
  - chemical shift (δ); units ppm
  - spin-spin coupling; coupling constants (J); units Hz
  - magnetic equivalence; symmetrical equivalence
  - dynamics
    - conformational exchange
    - chemical exchange
  - I= 1/2 nuclei ¹H, ¹³C: & ¹⁹F, ³¹P, ¹⁰³Rh, ¹¹³Cd, ¹⁹⁵Pt, etc.

C. Important Terms
- ligand - atom, ion or molecule bonded to a metal
- oxidation state - formal charge on a metal ion
- dⁿ configuration - number of valence d electrons
- coordination number - number of ligands directly bound to a metal
- first (inner) coordination shell - set of ligands bound directly to a metal
- second (outer) coordination shell - solvent or counter ions not directly bound to the metal
- electronic structure - the spatial and nodal character, electron population and energies of the orbitals (usually only the valence orbitals are considered) of an atom, ion or molecule
1. On the basis of electronegativities, state which member lower the polarizability. What influence does this pattern have on their boiling points?

2. State the electronic configuration and the number of unpaired electrons for each of the following gas phase ions: K\(^+\), Ti\(^{3+}\), Cr\(^{3+}\), Fe\(^{2+}\), Cu\(^{2+}\), Sb\(^{3+}\), Se\(^{2-}\), Sn\(^{4+}\), Ce\(^{4+}\), Eu\(^{2+}\), Lu\(^{3+}\).

3. The heavier atoms in any given group in the periodic table have larger inner cores, which lower the ionization potential of their valence electrons, but generally increase their polarizability. What influence does this pattern have on their boiling points?

4. On the basis of electronegativities, state which member of each pair is the more polar bond, and indicate the direction of the dipole. [Try to estimate relative electronegativities, and look up the numbers if needed.]

   C–N or N–O  P–S or S–Cl  Sn–I or C–I
7. Define the terms exothermic and endothermic for a physical or chemical process. What are the signs of \( \Delta H \) for each?

8. For a chemical reaction, what would be the significance of \( \Delta G^\circ < 0 \), \( \Delta G^\circ = 0 \), and \( \Delta G^\circ > 0 \)? What magnitude of the equilibrium constant (\( K \)) is associated with each case?

9. What is the conventional, arbitrary assumption made in defining the magnitudes of half-cell potentials (\( E^\circ \))? What is the convention for their signs?

10. The \( N-N \) bond energy in \( \text{F}_2\text{N} = \text{NF}_2 \) is only about 80 kJ mol\(^{-1}\) compared to 160 kJ mol\(^{-1}\) in \( \text{H}_2\text{N} = \text{NH}_2 \). Suggest a reason for this.

11. Some chemical reactions have two-term kinetic rate laws, for example:
\[
[\text{Pt(NH}_3)_3\text{Cl}]^- + \text{Br}^- \rightarrow [\text{Pt(NH}_3)_3\text{Br}]^- + \text{Cl}^- \\
\text{Rate} = k_1 [\text{Pt(NH}_3)_3\text{Cl}]^- + k_2 [\text{Pt(NH}_3)_3\text{Cl}]^- [\text{Br}]^-
\]
What does such a rate law imply about the reaction mechanism(s)?

12. Define the term isoelectronic and give examples for main group molecules and ions, and transition metal ions.

13. Use the Valence Shell Electron Pair Repulsion (VSEPR) Theory to predict the stable structures for: \( \text{PCl}_2\text{F}_3 \), \( \text{PCl}_2\text{Me}_3 \), and \( \text{SF}_4 \). In all cases the central atom is listed first and all other atoms are directly bound to it.

[Note: Although it is not covered in our standard introduction to VSEPR (as in Chem 6), the more electronegative group is often found in the axial position in trigonal bipyramidal structures like \( \text{PCl}_2\text{F}_3 \) and \( \text{PCl}_2\text{Me}_3 \). Several “explanations” of this observation, including hybridization and MO approaches, have been worked out, but we won’t cover them in this course.]

Describe the “ideal” central atom hybrids for each electron pair; any bond angle deviations from the ideal structure; and which molecules have non-zero dipole moments.

For each of the latter, identify the symmetry axis along which lies the molecular dipole.

14. Use VSEPR to predict the structures of the following molecules and ions. Indicate any deviations of bond angles from the ideal values.

\[
\text{BeF}_2 \quad \text{CH}_2 \text{ (singlet [no unpaired electrons])} \quad \text{OF}_2 \quad \text{PCl}_4^+ \\
\text{SO}_2 \quad \text{ClF}_2^+ \quad \text{BrF}_3 \quad \text{BrF}_5 \quad \text{SbF}_5 \quad \text{ICl}_4^-
\]

15. Predict the structure of HCP (C is the central atom) using VSEPR theory.

16. Using the 2s and 2p atomic orbitals as a basis set, prepare a "generic" molecular orbital (M.O.) energy level diagram for a homonuclear diatomic molecule. Use this diagram to predict the relative bond strengths and the numbers of unpaired electrons for the series of diatomics \( \text{O}_2^+, \text{O}_2, \text{O}_2^-, \) and \( \text{O}_2^{2-} \).

17. from Shriver + Atkins: Chapter 1 Exercises 9-11, 13, 16, 18, Problem 1.3; Chapter 3 Exercises 1-2, 4-7, 9, 10, Problem 1
1. **AO** \( n \) | l | m \\
--- | --- | --- \\
1s | 1 | 0,0 \\
2s | 2 | 0,0 \\
2p | 2 | 1, 0, 1, 1 \\
3d | 3 | 2, -1, 0, 1, 1 \\
4d | 4 | 2, -1, 0, 1, 1 \\
4f | 4 | 3, -3, -2, -1, 0, 1, 2, 3 \\

2. **Penetration** relates to the radial probability distribution of electron density in an atomic orbital, and the percentage of this distribution which is close to the nucleus and consequently feels a larger nuclear charge. Electrons in 3d orbitals are shielded from the full nuclear charge by core electrons \((1s, 2s, 2p)\) while \(3s\) and \(3p\) electrons have larger fractions of their electron density which penetrate the core and feel the nuclear charge. Thus, electrons in these latter orbitals are more stable (lower energy) than those in the 3d orbitals.

3. alkali metals: Li column; actinides: from Ac \((Z=89)\) through No \((Z=102)\); alkaline earth metals: Be column; halogens: F column; noble gases: He column; main group elements: B through He columns; d-block elements (aka transition metals): Sc through Zn columns, except not Y, La, or the 4th-row elements; f-block elements: those exceptions plus the elements in the part below the main table; lanthanides: La through Lu.

4. In forming ions, atoms will lose electrons from levels of highest principal quantum number, \(n\); with levels of equal \(n\), the electron will be lost from the orbital of highest \(l\). Electrons in degenerate orbitals will occupy orbitals singly to the maximum
permissible extent (Hund's rule of maximum multiplicity). These considerations lead to the following answers:

<table>
<thead>
<tr>
<th>Configuration</th>
<th># unpaired electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>K+(Ar)</td>
<td>0</td>
</tr>
<tr>
<td>Ti3+(Ar)3d1</td>
<td>1</td>
</tr>
<tr>
<td>Cr3+(Ar)3d3</td>
<td>3</td>
</tr>
<tr>
<td>Fe2+(Ar)3d6</td>
<td>4</td>
</tr>
<tr>
<td>Cu2+(Ar)3d9</td>
<td>1</td>
</tr>
<tr>
<td>Sb3+(Kr)4d10s2</td>
<td>0</td>
</tr>
<tr>
<td>Se2−(Ar)3d104s24p6</td>
<td>0</td>
</tr>
<tr>
<td>Sn4+(Kr)4d10</td>
<td>0</td>
</tr>
<tr>
<td>Ce4+(Xe)</td>
<td>0</td>
</tr>
<tr>
<td>Eu2+(Xe)4f7</td>
<td>7</td>
</tr>
<tr>
<td>Lu3+(Xe)4f14</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: for the transition elements (Z≥21) the energy of the (n–1)d level usually lies slightly below that of the ns level. Consequently ionization of the s electrons occurs before the d electrons. For lanthanoid and actinoid elements the f-level is the lowest-lying valence level. Thus transition metal ions always have a configuration [inert gas] ndm and f-block element ions always have [inert gas] nfm.

5. Increased polarizability leads to larger van der Waals forces (attractive interactions) between the atoms, and thus to a higher boiling point.

6. These are written with the more electronegative element 2nd, so the dipole (point positive charge) points that way.
   - CN > NO
   - S-Cl > P-S
   - Sn-I > C-I

7. Exothermic: giving off heat, ΔH < 0
   Endothermic: taking up heat from the surroundings, ΔH > 0

8. ΔG° = −RTlnK
   - ΔG° < 0: reaction proceeds forward spontaneously to equilibrium: K > 1
   - ΔG° = 0: reaction has no thermodynamic driving force: K = 1
   - ΔG° > 0: reaction proceeds backward spontaneously to equilibrium: K < 1
9. One half-cell is chosen as a reference and its \( E^0 \) is set at 0.000V; all others are referenced to it. Typically the standard reference is the standard hydrogen electrode: 
\[
\text{Pt/H}_2(1 \text{ atm})/\text{H}^+(1\text{M})
\]
The half-cell potential (or full cell potential) is related to \( \Delta G^0 \) by 
\[
\Delta G^0 = -nF E^0 \quad (n = \# \text{ of electrons transferred}; \ F = 1 \text{ faraday}).
\]
Therefore,

a \( +E^0 \) ensures a \( -\Delta G^0 \) and a spontaneous forward reaction  
a \( -E^0 \) ensures a \( +\Delta G^0 \) and a spontaneous reverse reaction  
Half-cell reactions are written as reductions, thus the more positive the value of \( E^0 \), the more easily the reactant is reduced.

10. Two arguments can be used, both of which lead to the same conclusion: first, the lone pairs on F atoms attached to one N atom will repel those on F atoms on the adjacent N, serving to destabilize (and weaken) the N-N bond (relative to \( \text{H}_2\text{N-NH}_2 \)); second, the strong electron-withdrawing F atoms will withdraw electron-density from N leading to a weaker N-N bond.

[Both these arguments affect the relative energies of the reactant side of the equation for dissociation of the N-N bond: 
\[
\text{R}_2\text{N-NR}_2 \longrightarrow 2 \text{R}_2\text{N}^- \quad \text{R = H or F}
\]
You should also think about how H and F would affect the relative stabilities of the products of this dissociation, since both sides will affect the magnitude of \( \Delta H_{\text{reaction}} \).]

11. The reaction is a nucleophilic substitution of \( \text{Cl}^- \) by \( \text{Br}^- \), occurring at a Pt atom. A 2-term rate law implies that 2 different mechanisms are operating: the first has a rate constant \( k_1 \) and its rate is (apparently) dependent only on \([\text{Pt(NH}_3)_3\text{Cl}]^-\); the 2nd has a rate constant \( k_2 \) and its rate is dependent on both \([\text{Pt(NH}_3)_3\text{Cl}]^- \) and \([\text{Br}^-]\). Depending on the magnitudes of \( k_1 \) and \( k_2 \), one path may dominate or both may contribute significantly to the overall observed reaction rate.  
[You probably haven’t seen this before, but that’s OK; we will discuss this type of reaction and rate law in more detail later in the term.]  

12. Atoms, ions or molecules are isoelectronic if they contain the same number of electrons:  
e.g. \( \text{Ti}^{3+} \) and \( \text{V}^{4+} \), \( \text{CO} \) and \( \text{NO}^+ \)  
This strict definition is frequently loosened to allow 'isoelectronic' to include only the valence electrons of the atoms or ions.  
e.g. \( \text{XeF}_4 \) and \( \text{ICl}_4^- \), \( \text{Co}^{3+} \) and \( \text{Pt}^{4+} \).
13. 

\[
\begin{align*}
\text{dipole axis} & :<90^\circ \\
\text{F} & - \text{Cl} - \text{F} \\
\text{Me} & - \text{P} - \text{Me} \\
\text{S} & - \text{F} - \text{F} \\
\text{dsp}^3 & >120^\circ \\
\text{lone pair equatorial}
\end{align*}
\]

<table>
<thead>
<tr>
<th>more electronegative group axial</th>
<th>no dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>no deviations from ideal geometry</td>
<td></td>
</tr>
</tbody>
</table>

Note: for trigonal bipyramidal structures like this, the more electronegative group is often found in the axial position. Several “explanations” of this observation, including hybridization and MO approaches, have been worked out, but we won’t cover them in this course.

14. 

\[
\begin{align*}
\text{F-Be-F} & :180^\circ \\
\text{H-C-H} & :<120^\circ \\
\text{F-O-F} & :<109.5^\circ \\
\text{Cl-P+Cl} & :109.5^\circ \\
\text{O=O} & :<120^\circ \\
\text{F-Cl-F} & :<109.5^\circ \\
\text{F-Br-F} & :<90^\circ \\
\text{F-Sb-F} & :\text{angles }<90^\circ \\
\text{Cl-Cl-Cl} & :\text{no deviations from 90, 120° angles} \\
\text{Cl-Cl-Cl} & :\text{square planar, 90° angles}
\end{align*}
\]

15. VSEPR predicts H-C≡P: (just like HCN).
16. The diagram shows electrons filled in for the O\(_2\) molecule. 12 valence electrons, 2 unpaired. Bond order = 1/2 (#bonding electrons – # antibonding electrons) = 1/2 (8–4) = 2.

![Diagram of O\(_2\) molecule with p\(\sigma\) and p\(\pi\) orbitals](image)

Similar analysis for cation and anions:
- O\(_2^+\): 1 unpaired electron, BO = 2.5
- O\(_2\): 2 unpaired electron, BO = 2
- O\(_2^-\): 1 unpaired electron, BO = 1.5
- O\(_2^{2-}\): 0 unpaired electrons, BO = 1

The bond strength increases with bond order; this is a general result for bonds between 2 identical atoms.
Problem 1.3.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic Configuration</th>
<th>I(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>[Kr]5s(^1)</td>
<td>4.18</td>
</tr>
<tr>
<td>Ag</td>
<td>[Kr]4d(^{10})5s(^1)</td>
<td>7.57</td>
</tr>
</tbody>
</table>

H atom ionization energy = \(E_{\text{final}} - E_{\text{initial}} = E_{\text{infinity}} - E_n = -E_n\) (since \(E_{\text{infinity}} = 0\))

\[-(\frac{hcR}{n^2}) = 13.6\text{eV}/n^2\] (see text, page 19)

For \(n = 4\), \(E = 0.85\) eV

For \(n = 5\), \(E = 0.54\) eV

These values are much lower than those for Rb and Ag!

Despite considerable screening of valence electrons by core electrons, and despite electron-electron repulsion, \(Z_{\text{eff}}\) is so much larger for Rb and Ag than for H that it takes an order of magnitude more energy to remove the most loosely bound electron. [N.B. we have kept the \(1/r\) component constant for each comparison.]

From the textbook

Page 8, Exercise 1.11. The last line refers to the "special stability of half-filled subshell configurations." Although many textbooks comment on this (and make similar comments on filled shells), they are avoiding a better explanation, based on \(Z_{\text{eff}}\), electron-electron repulsion, etc. See also #s 1.13 and 1.15 for similar comments, and please don’t give this kind of answer on your exams.

Problem 3.1

Table 3.4 (p. 71) illustrates the clear trend of increasing covalent radius on descending a group. The valence electron configuration remains constant for each group member, but \(Z_{\text{eff}}\) felt by the valence electrons actually increases as we descend the group. But \(1/r\) decreases because the valence orbitals are of higher \(n\). This factor dominates, and the covalent radius increases. On traversing a period, we populate valence orbitals of the same \(n\), and \(Z_{\text{eff}}\) increases, so we expect a smaller radius as the increasing \(Z_{\text{eff}}\) contracts the orbitals.