What is Chem 5?

- Course title: "**Scientific Computational Skills for Chemists**"
- Lecture (3 hr); discussion (1 hr); computer laboratory (2 hr).
- Catalog: *"Introduces students to the personal computing software used by chemists for managing and processing of data sets, plotting of graphs, symbolic and numerical manipulation of mathematical equations, and representing chemical reactions and chemical formulas. Co-requisites: Chemistry 1C or H2C, and Mathematics 2D. Prerequisites: Chemistry 1A-B or H2A-B, and Mathematics 2A-B."*
- Chem 5 is **required** for all chemistry majors
- 2007-2008: Offered in F, W, SSI, SSII quarters
- 2008-2009: Offered in F, S quarters (summer session is still undecided)

Where is Chem 5 taught?

- Lecture and laboratory take place in the instructional computing labs, which are limited in sitting capacity (because of the number of available PC terminals) to:
  - MSTB Lab B: 48 students and 1 instructor
  - MSTB Lab A: 46 students and 1 instructor
- The class size is usually set at 44 students to allow for the possibility of having several broken terminals
- Software that Chem 5 students need is installed only in MSTB Lab B (MathCAD, ChemDraw, SciFinder, and Spartan)
- Lab A has only MS Office

- Chem 5 class size can be increased to about 90 students if:
  - Both Lab A and Lab B are used in parallel (doable, although places an unreasonable load on the instructor)
  - MathCAD and ChemDraw are installed in Lab A (Spartan is not currently in use)

Why do we need Chem 5?

General needs

- Overall computer literacy (which is lacking!!!); searching information on chemical properties and reactions; scientific literature search; preparation of scientific graphs; inserting graphs into word-processing documents;

Theoretical physical chemistry needs (130, 131)

- Matrix (e.g., eigenvalue) problems; integration and differentiation of functions; plotting functions in 2D and 3D space; calculations involving units; etc.

Experimental physical chemistry needs (153)

- Fourier-transform; non-linear fitting of data; filtering data; basics of programming

Analytical chemistry needs (151, 151L, 152)

- Complex equilibria calculations; statistical analysis of data; linear fitting; importing, exporting, and manipulating tabular data;

Synthetic chemistry needs (51, 51L, 107, 107L, 125, 160, …)

- Drawing complicated chemical structures and reactions; predicting NMR shifts; predicting peaks in mass-spectra; etc.

How computer-literate are our students?

Informal surveys of entering Chem 5 students show that

- Very few of them know where to look for scientific information
- Only 1-2 students are familiar with programs like MathCAD, Mathematica, Maple, Matlab, etc.
- Usually, none of them are familiar with programming languages like C++, Fortran, Java, etc.
- Only about a third of them can do rather elementary calculations in spreadsheet applications like Excel

The goal of Chem 5 is to remedy these obvious deficiencies in computer training

How are these needs satisfied by Chem 5?

Program	Useful for:	Sergey's syllabus	Craig's syllabus	Ken's syllabus
MathCAD	130, 131, 153	7 weeks	9.5-10 weeks	7 weeks
Excel	151, 151L, 152, 170	1.5 weeks	-	1 week
ChemDraw	51, 51L, 107, 107L, 125, 160	0.5 weeks	-	1 week
SciFinder, web-of-science, CRC handbook, etc.	All upper division courses; 180	1 week	0-0.5 weeks	1 week
Spartan	130, 131, 135, 137, 138	Annoying bugs in the program – gave up using it	-	-

Sample problems illustrating the skills students are supposed to acquire in Chem 5

Example of a physical chemistry problem

(solved with MathCAD)

Last week, we went through the logic of how to integrate the area of a circle using Monte Carlo statistics. Unlike “normal” integration, extension of Monte Carlo integration to more dimensions is rather easy. For instance, to do a sphere instead of a circle, you would just do the same thing for the z coordinate that you did for the x and y coordinates. This makes it possible to think about “spheres” in multiple dimensions. So, your job this week is to determine the volume of a 4-D sphere. Remember, the equation for the area of a circle is πr^2. The volume of a 3-D sphere is (4/3) πr^3. What is the volume of a 4-D sphere? It should be of the form $V_{4D} = A\pi r^4$, but what is the value of A? Determine A with a standard deviation less than 1% of A by performing several Monte Carlo calculations a performing a statistical analysis of the results.

Advanced students: derive the value of A analytically, and compare it to your numerical result.

Example of a physical chemistry problem

(solved with MathCAD)

The radial wavefunctions for a hydrogen atom have the following functional form. In these equations, r is the distance between the electron and the nucleus; ρ is the normalized distance; Z is the nuclear charge (Z = 1 for hydrogen atom); and a_0 is the Bohr radius.

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \exp(-\rho)$$

$$\Psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (2-\rho)\exp\left(-\frac{\rho}{2}\right)$$

$$\Psi_{3s}(r) = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(27-18\rho+2\rho^2\right)\exp\left(-\frac{\rho}{3}\right)$$

where

$$\rho = \frac{Zr}{a_0} \qquad a_0 = 5.2918\times 10^{-11} m$$

From quantum mechanics, one can calculate the probability of finding the electron in the distance range $r_a < r < r_b$ and the average distance from the nucleus as follows:

$$p(r_a < r < r_b) = \int_{r_a}^{r_b} \left[\Psi(r)\right]^2 2\pi r^2 dr \qquad \langle r \rangle = \int_0^{\infty} r\left[\Psi(r)\right]^2 2\pi r^2 dr$$

Use these equations to calculate for 1s, 2s, and 3s states of the hydrogen atom:

1. The probabilities that the electron is in the distance range $0 < r < a_0$ from the nucleus.
2. The average distances from the nucleus
3. Express the average distances in the multiples of Bohr radius

Example of a physical chemistry problem

(solved with MathCAD)

The number of collisions a given molecule experiences every second in gas-phase can be calculated as follows:

$$z = \rho \cdot \sigma \cdot \upsilon_{rel} \quad \text{where relative velocity is:} \quad \upsilon_{rel} = \left(\frac{16kT}{\pi m} \right)^{1/2}$$

1. Calculate the relative velocity, υ_{rel}, and the number of collision per second, z, for a nitrogen molecule (molecular weight = 28 g/mol) based on the information provided in the table below.

2. Report z in the units of s^{-1}. Report υ_{rel}. in units of cm/s.

Parameter (unit)	***Explanation***	***Information provided to you***
T (K)	Absolute temperature	25 degrees Celsius. (Needs to be converted to Kelvin.)
k (J/K)	Boltzmann constant	Look up the value online
σ (m^2)	Collision cross section	0.4 nm^2
ρ (m^{-3})	Number concentration	2.4×10^{19} cm^{-3}
m (kg)	Mass of <u>one</u> N_2 molecule	Molecular weight (28 g/mol) is provided instead of the mass. Hint: avoid using “m” for variable name as “m” is reserved for “meter” in MathCAD.

Example of an analytical chemistry problem

(solved with Excel)

A chemistry student prepared several calibration solutions by diluting an aqueous stock solution containing 100 ppm of Cu and 100 ppm of Zn (ppm = part per million by weight). Student used AAS (atomic absorption spectroscopy) to measure absorbances of all calibration solutions at wavelengths corresponding to a Zn atomic line and to a Cu atomic line. Results of these measurements are given below. Student then took 0.1 g of an unknown metal alloy and dissolved it in 100 mL of acid. 5 mL of the resulting solution was taken and further diluted with water to 50 mL. AAS measurements on this diluted solution gave results shown in the table below. What was the weight percentage of Zn and Cu in the unknown metal alloy?

Solution	Volume of stock solution (mL)	Diluted with water to: (mL)	Zn absorbance	Cu absorbance
Blank	0	50	0.033	0.013
Calibration 1	0.5	50	0.081	0.035
Calibration 2	1	50	0.136	0.062
Calibration 3	1.5	50	0.169	0.077
Calibration 4	2	50	0.239	0.109
Calibration 5	2.5	50	0.275	0.133
Diluted unknown	-	-	0.110	0.120

Example of an analytical chemistry problem

(solved with MathCAD)

The following equilibria take place in the solution of your old friend oxalic acid:

$$H_2C_2O_4 \Leftrightarrow HC_2O_4^- + H^+ \qquad K_1 = \frac{[HC_2O_4^-][H^+]}{[H_2C_2O_4]} = 0.056\ \mathrm{M}$$

$$HC_2O_4^- \Leftrightarrow C_2O_4^{2-} + H^+ \qquad K_2 = \frac{[C_2O_4^{2-}][H^+]}{[HC_2O_4^-]} = 5.4\times10^{-5}\ \mathrm{M}$$

$$[ALL] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$$

1. Assuming that [oxalates] = 0.1 M, plot the concentrations of [$H_2C_2O_4$], [$HC_2O_4^-$], and [$C_2O_4^{2-}$] in the same graph as a function of pH over the pH range of 0-8.

2. What is the value of pH in a 0.1 M solution of oxalic acid ([ALL] = 0.1M)? To solve this problem, use the charge balance equation and rewrite it in such a way that only [H^+], [ALL] and equilibrium constants remain. Use root() to solve the resulting equation for [H^+]. Here is the charge balance equation (for simplicity, it neglects [OH^-] and self-ionization of water):

$$[H^+] = 2\times[C_2O_4^{2-}] + [HC_2O_4^-] + [OH^-]$$

Example of a chemistry database problem

(solved with CRC and Knovel)

Search either Knovel (Lange's Handbook of Chemistry is the most useful section of Knovel for chemists) or CRC Handbook to find the following information. Place your answers in the following table. Be sure to include the units; numbers without specifying the units will be treated as incorrect. If the number is unitless, write “unitless”.

Question	**Value**	**Units**
Example: Heat capacity of benzoic acid	*152.78*	*J/(mol K)*
Vapor pressure of pure liquid H_2O at T = -8 °C		
Solubility of NH_4Cl (ammonium chloride) in water at T = 80 °C		
Vapor pressure of H_2O above a 25 wt% solution of NaCl at T = 0 °C		
Viscosity of anhydrous ethanol at T = 20 °C		
Refractive index of acetonitrile at room temperature		
Boiling point of deuterated acetone, $CD_3C(O)CD_3$		
Melting point of Bicyclo[2.2.1]-2-heptene		
Enthalpy of vaporization of $HgCl_2$		
Enthalpy of sublimation of I_2 (iodine)		
Standard enthalpy of formation of 2-Butyne		
Natural isotopic abundance of ^{34}S		
Standard electrochemical potential for half-reaction: $TeOOH^+ + 3H^+ + 4e^- = Te + 2 H_2O$		
Ionization potential of bromoethane		
Heat of combustion of pyrene ($C_{16}H_{10}$, , CAS 129-00-0)		
Surface tension of methanol		

Examples of chemistry database problems

(solved with web-of-science)

A. Roughly 25 years ago, UCI Chemistry professor A.J. Shaka published a very important paper on nuclear magnetic resonance that was cited more than a thousand times by other researchers. Here is what we know heard this paper:

Published sometime around 1984 (plus or minus one year) by A.J. Shaka and others

1. Use Cited Reference Search in the Web-of-Science to locate this reference, and find out how many times this particular publication has been cited by other researchers.
2. Find the latest publication that appeared in the Journal of Biomolecular NMR and cited the Shaka's paper in question. Use the same format for your answers as described in problem 1 above. Do not use "et al." to truncate the list of authors; you must include a complete list.
3. Provide a pdf link to both of these papers
4. Briefly explain what kind of information Figure 1 of Prof. Shaka's paper conveys.

B. (this problem is obviously a couple of years old) Find the first scientific publication of our Chemistry Department Chair, Professor V. A. Apkarian. Give the title of the article, the journal, the co-authors, the date of publication and where the work was performed.

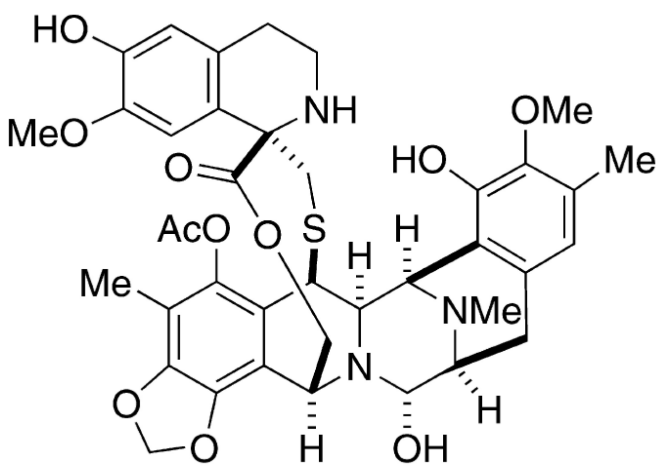
C. Find data for the vapor pressure versus temperature for propane over the range 140 K to 190 K. Make a plot of the data. Make a polynomial fit of the data, using enough terms to obtain a good fit. Use your equation to predict the boiling point of propane. Compare to the actual value.

Example of ChemDraw problem

(solved with ChemDraw, obviously)

The following image of Trabectedin (also known as ecteinascidin 743 or Et-743), a promising Cancer drug, was taken from Dan Fishlock and Robert M. Williams “Synthetic Studies on Et-743. Assembly of the Pentacyclic Core and a Formal Total Synthesis” J. Org. Chem., 2008, 73 (24), pp 9594–9600.

- Reproduce this image in ChemDraw as closely as possible. It does not have to look exactly the same but all the bonds, atoms, and functional groups must be in the correct positions.
- Use Analysis Window to calculate and display Chemical Formula and Molecular Weight values under the image.
- Copy your image from ChemDraw, including the analysis results, and paste it below.



Example of a Spartan problem

(solved with ChemDraw, obviously)

Start with the ammonia molecule. Build the molecule and optimize the geometry (find the equilibrium geometry) using the Hartree Fock method and the 6-31g basis set. Report the bond lengths and bond angles. Use Chem. Draw to illustrate the results. Finally, calculate the highest occupied molecular orbital, HOMO. From its shape, and your knowledge of the ammonia Lewis Structure, give a descriptive name to this orbital. Also, report the total energy of the molecule.