MOLECULAR MODELING AS A SELF-TAUGHT COMPONENT

of a Conventional Undergraduate Chemical Reaction Engineering Course

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We have used the popular molecular-modeling program Gaussian as the basis for undergraduate student projects that reside within a conventional chemical reaction engineering course that follows the latest of H.S. Fogler's widely used texts.[1] (Our choice of Gaussian over several similar programs was based solely on our existing site license.)

The educational objectives for the students were:

1. *To learn unfamiliar concepts and techniques primarily from Internet resources and to use those to do Gaussian-based calculations on a chemical kinetics project of their choice,*
2. *to gain an appreciation of the relationship between molecular properties and macroscopic concepts such as internal energy, enthalpy, rate constants, and activation energies, and to be able to think on a molecular level, and*
3. *to retain a memory of this pictorial do-it-yourself project, and some of its lessons, longer than they would by studying the contents of one more chapter of a text.*

Fogler's text[1] carefully develops an algorithm for chemical reaction engineering, in a five-chapter sequence, which is: Mole Balance + Rate Laws + Stoichiometry + Energy Balance + Combine. At that sequence's conclusion, students are provided with, and should be able to solve, a number of reaction engineering problems from former California… Professional Engineers-Chemical Engineering Examinations. We have followed this well-designed sequence at Wayne for many years.

Reaction rates are defined in Fogler's text as algebraic functions of rate constants, k, and chemical species, i, and concentrations, c_i. For example, in an irreversible second-order reaction between species B and C, the reaction rate would be kc_Bc_C. The temperature dependence of k is given by the familiar Arrhenius equation, *i.e.*, $k = A\exp(-E_a/RT)$, where A is the "frequency factor" and E_a the "activation energy." This works well in Fogler's algorithm for design when appropriate values for k, A, and E_a are available. But when they are not, one may obtain them from experiments or from theoretical calculations. Each of these choices has advantages and disadvantages.

Fogler and his associates recognized the value of molecular modeling and, in 2004, added an excellent "Web Module"[2] to the text's website that describes modeling's value, its methods, and its applications. They state there that

> *"For chemical engineers, molecular modeling calculations are most useful in determining kinetic and thermodynamic properties of a reaction system. The next generation of chemical engineers will rely heavily on molecular modeling and quantum mechanical calculations to design reactions to produce pharmaceuticals, industrial chemicals, and complex molecules."*

Erhard Rothe *retired in May 2015 as a professor from the Chemical Engineering and Materials Science Department at Wayne State University after serving since 1969. He has 205 publications that have been cited 3,900 times. These have been mainly in molecular-beam studies of collisions, laser diagnostics of combustion, and laser interactions with materials.*

William Zygmunt *graduated from the Chemical Engineering and Materials Science Department at Wayne State University in 2015 and was a graduate student at the University of Michigan in the Fall of 2015. He has carried through several undergraduate projects with Professor Jeffrey Potoff in the field of molecular dynamics and simulation.*

But when we communicated with three of that Web Module's authors, we learned that they did not know whether this material had been previously applied in an undergraduate chemical engineering course. Based on the Web Module's content, we concluded that the modeling was doable for our students and should be interesting to most of them.

OUR USE OF GAUSSIAN

We installed Gaussian 09 on PCs in the Engineering College's computer lab and in our AIChE student room. Gaussian's website says that "From the fundamental laws of quantum mechanics, Gaussian 09 predicts the energies, molecular structures, vibrational frequencies, and molecular properties of molecules and reactions in a wide variety of chemical environments. Gaussian 09's models can be applied to both stable species and compounds which are difficult or impossible to observe experimentally (*e.g.*, short-lived intermediates and transition structures)." The program will yield molar thermodynamic functions for both stable species and activated complexes. In reaction kinetics, we can use those functions to calculate rate constants and activation energies.

We also installed GaussView 5, the graphical user interface that prepares input for submission to Gaussian and graphically displays its output. The Gaussian website claims that "setting up calculations is simple and straightforward, and even complex techniques are fully automated."

We first checked whether the program's use was feasible for our inexperienced students. One of us, the equally inexperienced ER, had never done such modeling. He started by watching three YouTube videos,[3] whose total running time was about 47 minutes, in which Prof. Jeff Yarger of Arizona State University provided clear instructions. Within about three hours ER could operate the program well enough to do simple versions of problems that students might select and concluded that students should be able to do the same. The other author (WZ) acted as coordinator for the project. It was a bit of luck that WZ was simultaneously enrolled in a chemistry course on molecular modeling by means of Gaussian software.

Our approach

There were 32 students in our 4-credit junior-level (CHE3400) class. A comparison with the previous years' students, based on quizzes and exams, indicated that they were a typical chemical reaction engineering class at Wayne. They formed teams of four students. Seven of these teams participated in the Gaussian projects. One team had competed in Chem-E-Car and was allowed to report on chemical kinetics related to that.

Except for a 30-minute explanation of the project on the first day of class, the remainder of the semester's class time was entirely devoted to conventional chemical reactor engineering as defined by following Fogler's book, and lecturing on those topics.

Those opening 30 minutes consisted of (a) a semi-qualitative presentation of the plausibility of the Boltzmann distribution of energies in a material as the one that will yield the most combinations of molecular energies and (b) an explanation that Gaussian uses that distribution of energies, and the calculated molecular properties, to find the molar enthalpy (and internal energy, entropy, and free energy). Finally students were directed to the three YouTube links[3] that had enlightened ER.

A progress check on the semester-long project was a hand-in that was due one month after the first class. That assignment was a Gaussian calculation of the enthalpy change, ΔH_{rxn}, occurring for a reaction of their choice and a comparison of that result with an experimental literature value. In order to increase participation among team members, we gave advance

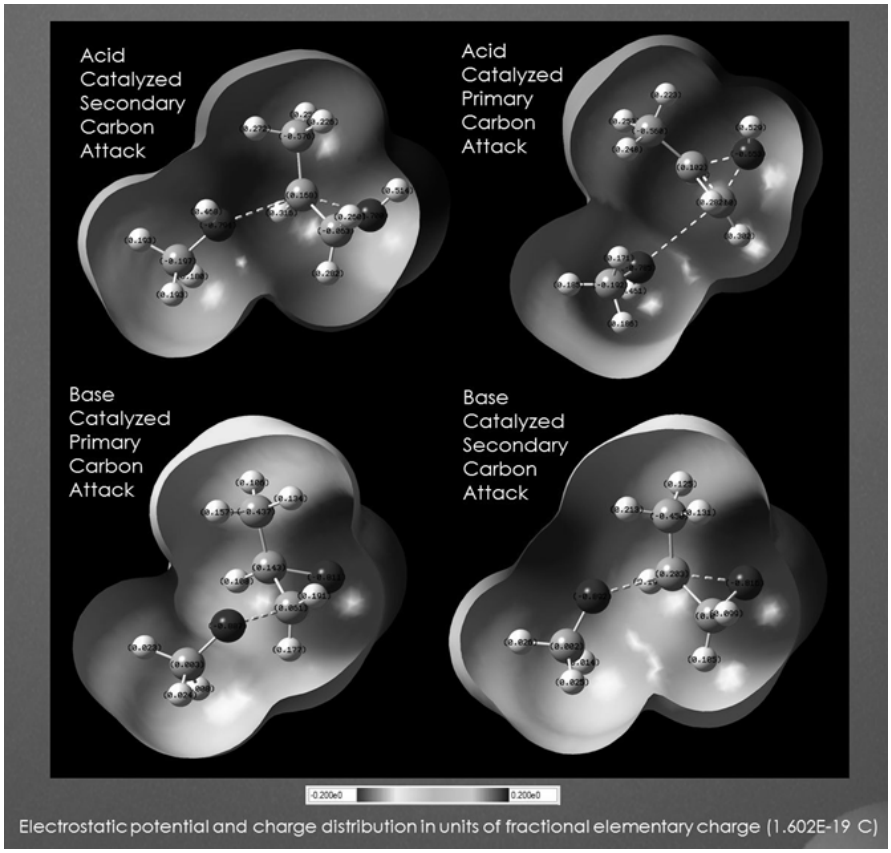

Figure 1. *A poster picture from Acid vs. Base Catalyzed Ring Opening of Epoxide.*

notice that there would be a question on the midterm exam whose answer would be simple for anyone who had carried through the ΔH_{rxn} calculation.

The kinetics usually required a calculation of transition state energies. Transition structure calculations are trickier than those for stable molecules and require a combination of good guesses and appropriate choice of basis sets in order to allow the program to compute them.

The final class period was a poster session describing teams' results that was graded by a combination of faculty and students. The faculty were from chemical engineering and did not know this modeling technique. The student judges were graduate students who did know it: some were from chemistry whose theses were primarily based on Gaussian. Figures 1 and 2 show some sample results extracted from the posters.

One of us (WZ) was in charge of the project, made sure the programs were properly installed, provided some help to students who contacted him, and organized the poster session.

Except for the Chem-E-Car students, every other team presented a poster in which reaction kinetics were calculated from Gaussian. All of these poster titles are presented in Appendix 1. There are clearly differences in topics and in the complexity of the self-assigned problems. The chemical engineering faculty judges were generally pleased with the outcomes and so were the judges from chemistry.

DISCUSSION

For many years we have included a student project in the course. Each previous year we chose one or two topics from a number of interesting Fogler-based topics that are contained in his Web Modules.[4] We asked students to devise, and carry through, some creative project around such Fogler-based subjects as cobra bite remediation and modeling of hippopotamus

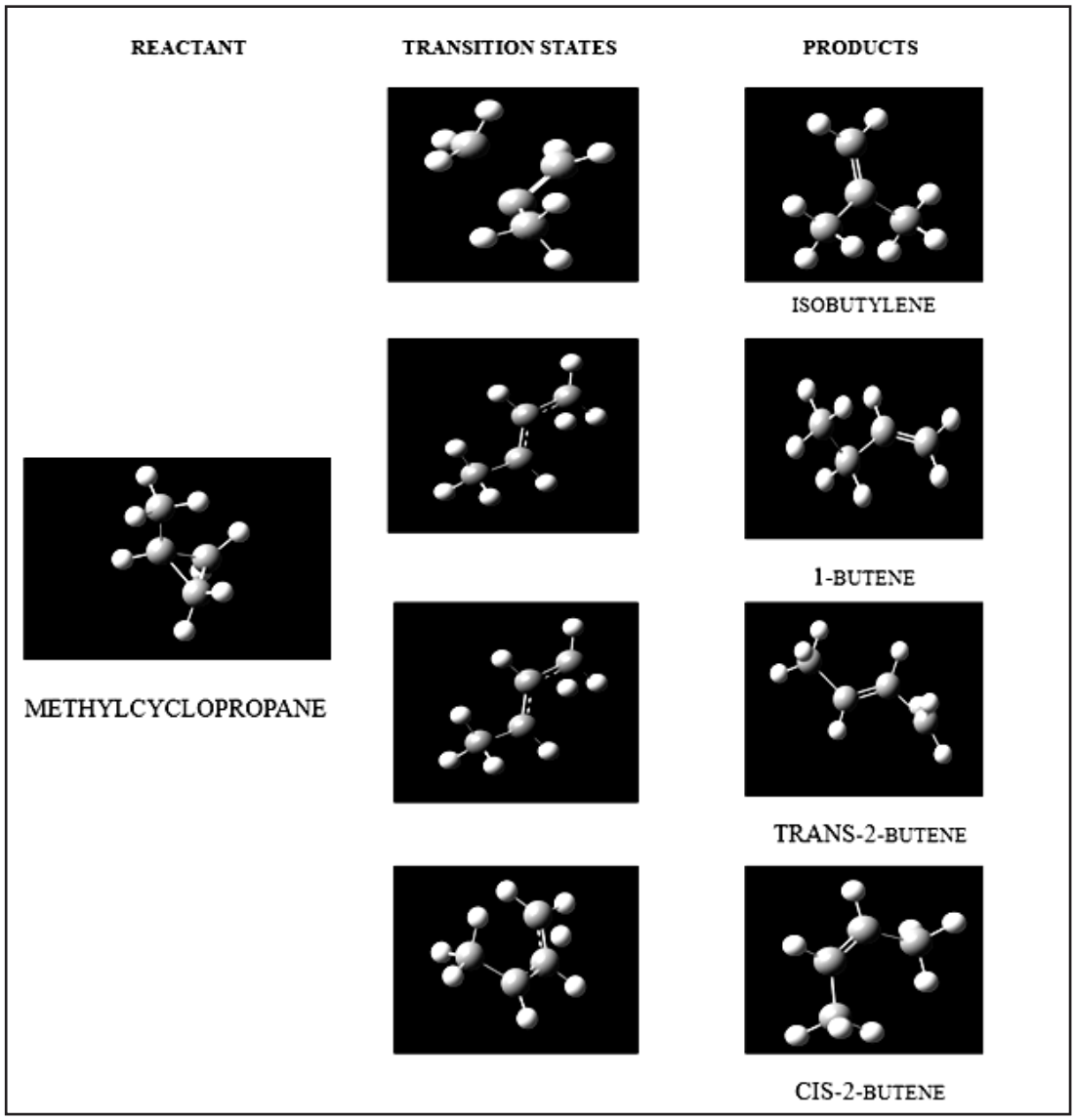

Figure 2. *Poster picture from The Unimolecular Thermal Isomerization of Methylcyclopropane.*

digestive systems. There is an element of conflict between creativity and guidelines. We have always told students that a major portion of their project grades would be based upon creativity.

The Gaussian project required more self-study and work than those previous subjects, and so we eliminated the study of one chapter of Fogler's text that had previously been taught. R.M. Felder's[5] article made us feel better about that. We believe that students are going to retain much more from watching a monitor while creating and then optimizing molecular structures (with the aid of great graphics), and then successfully relating those to real parameters than from either, say, cobra bites, or about the chapter of Fogler that was not taught.

In this project we did not assign reactions to be studied but rather allowed the students to find a balance between a topic of interest to them and the ability to carry it out given the available time, skill, and the indifferent PCs that were available.

CONCLUSIONS AND SUGGESTIONS FOR POSSIBLE FUTURE USE

We considered this experiment to be an initial success. We wanted students to learn on their own, although possibly still better technical results and still better-quality posters would have been produced with more class time devoted to the subject. But we were reluctant to stray too far from a conventional reactors course.

We chose to have a short lecture on the basis of Gaussian, but after that did not dwell on the science involved in the software. We thought it was adequate to simply acquire the skill to use it. That choice is debatable and our view is that for this course, the ability to use it is enough.

There is no reason that this material has to be done as a project except for the tradition that we had in this course in prior years.

It would probably help to have some of these Gaussian methods introduced in a prerequisite thermodynamics course so that students will gain an appreciation of the fundamental basis of internal energy (and of entropy and the free energy functions). Then that basis would allow only the kinetics calculations to be added to the chemical reaction engineering course. The only disadvantage to that suggestion is that two instructors would need to have a similar outlook. (At Wayne, this year, the same instructor is going to teach thermo and reactors in sequence and may apply this idea.)

Similar arguments would seem to suggest the value of such modeling calculations in graduate thermodynamics and/or reaction engineering courses.

For any of these suggestions, a chemical engineering instructor has to ask himself/herself: Is it worth it for me, and for the students, to learn how to do this? And, if so, what previously beloved material can I let go of?[5]

ACKNOWLEDGMENTS

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APPENDIX 1 – TITLES OF STUDENT PROJECTS

- Gaussian-Hydrogenation (of three cycloalkanes)
- Energy and Enthalpies Calculations for a S_N2 Reaction via Gaussian Software
- Salicylic Acid Synthesis and Inhibition of Prostaglandin Formation in Cyclooxygenase
- Regioselectivity of Acid vs. Base Catalyzed Ring Opening of Epoxide
- The Unimolecular Thermal Isomerization of Methylcyclopropane
- Theoretical Examination of the Diels-Alder Reaction of 1,3-Butadiene with Cyclopentadiene
- Energy Calculations for Uracil and its Isomers Using Gaussian Software
- Chem-E Car Kinetics

APPENDIX 2 – STUDENT COMMENTS

We did a three-question survey after the final poster sessions. Due to space limitations we present here all the answers (unedited) to only the first one.

1. In a few words, what are your general thoughts about the project assignment?

- *Interesting project, I wonder if it can be applied to industry?*
- *Good project, but a lot of work involved*
- *Helpful project with good applications*
- *A neat program but somewhat difficult to learn the software*
- *Fun and interesting, I learned a lot about what Gaussian can do*
- *Project felt like busywork to compensate for material covered in class*
- *Too broad of a project, I couldn't pay as much attention to detail as I wanted to*
- *Interesting experience*
- *I wanted to know more about what was expected of us before I pick a topic next time*
- *A good experience for discovery and computation*

- *Project was too vague, I needed more guidance on what was acceptable*
- *Interesting approach to a new topic and software*

2. Do you feel that the project was too difficult or too easy? On a scale of 1(easy) to 5 (hard), the average was 3.0.

3. Do you feel that you had good advising on this project? On a scale of 1 (bad advising) to 5 (good advising), the average was 3.7.

ER also talked to almost all of the students about three months after the course finished. No one appeared to have forgotten the project. The major themes brought up were that (a) some felt it was initially too hard and would have liked more instruction, (b) some felt that because the rate constants calculated are only a portion of a real reactor design, it may have been overkill, but (c) many felt that it was a good experience and thought that such calculations are going to become commonplace in the profession.

ER's research career has been essentially based on experimental results. Nevertheless he thinks that the present trend of supplanting some experiments with (usually cheaper) calculations will continue and that such modeling is going to become a norm among chemical engineers.

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