Development and Dissemination of Mathcad Templates for Physical Chemistry Education

Theresa Julia Zielinski*
Monmouth University, West Long Branch, NJ
and
Michael P. Barnett†
P.O.Box 322, Princeton, NJ 08542-322

August 6, 2003

Introduction

The mission of the Physical Chemistry Mathcad Document site (PCMS) to support undergraduate and early graduate instruction in physical chemistry includes the use of symbolic computation. The site provides modules for a rich variety of instructional topics contributed by a growing community of chemistry educators. Many of the modules use the symbolic computation feature of Mathcad. One author of this note (TJZ) initiated the site, directs its maintenance, and has written many of the modules. The other author (MPB) began the note as a summary of the site material to support a short verbal presentation in the Chemistry and Computer Algebra workshop during the 2003 annual meeting of the International Symposium on Symbolic Algebraic Computation (ISSAC) because TJZ could not attend. At the suggestion of TJZ, the note is being iterated under joint authorship. The present "minimalist" version was produced on August 6th.

List of topics covered by individual modules

1. stoichiometry
   (a) [34] deals with pH and ionic equilibria.
2. gas laws
   (a) [19] introduces the basic gas laws.
   (b) [63] fits van der Waals and Redlich–Kwong formulas to data. It uses sum of squares deviations (SSD), the F-test, Hessians and symbolic differentiation.

*tzielins@monmouth.edu
†michaelb@princeton.edu

3. classical thermodynamics

    (a) [65] discusses the standard state of a real gas and the quantification of departures from ideality. It considers change of enthalpy with temperature and pressure, the Redlich-Kwong equation, imperfection, the Joule–Thomson coefficient, standard internal energy and enthalpy. These are illustrated by data for sulfur dioxide.

    (b) [10] discusses the Gibbs free energy of a reacting system and the issue of spontaneity.

    (c) [6] combines the consideration of classical thermodynamics, statistical mechanics and quantum mechanics. It distinguishes work and heat at the molecular level, considers disorder, introduces the Boltzmann distribution law, and uses the particle in a box as part of an example.

    (d) [12] explores the asymptotic behavior of stepwise irreversible isothermal expansion and compression.

    (e) [26] explains the Carnot cycle. It contrasts the results of numerical and symbolic integration, bases calculations on the ideal gas and van der Waals models for methane, and discusses adiabatic expansion.

    (f) [20] discusses the third law entropy of lead.

    (g) [39] is an adiabatic flame study to determine the temperature of the combustion flame of n-butane in air.

    (h) [50] computes a liquid–vapor phase diagram for a binary system. Raoult's law is used in the treatment assuming ideal gas behavior, and the van Laar equation is used for non-ideality. Activity coefficients, phase diagrams and azeotropes are discussed.

4. chemical kinetics

    (a) [14] provides an extensive introduction to the basic principles of reaction rates, mass balance, reversibility and irreversibility. It covers the steady state approximation, and considers numerous two and three species systems. Attention is given to numerical instability, to the application of l'Hospital's rule and to a comparison of analytical and numerical solutions.

    (b) [2, 5] provide very concise accounts of the introductory ideas of chemical kinetics.

    (c) [40] discusses Lotka-Volterra, Brusselator, Oregonator and Belousov-Zhabotinsky systems. It introduces the ideas of phase plane and phase portrait, oscillators, attractors. It gives examples of evolutionary and oscillatory systems and points to further reading.

    (d) [29] discusses the effect of pH on enzyme kinetics.

    (e) [1] focuses on economics of optimizing a chemical process.

    (f) [27] models the kinetics of ozone in the stratosphere involving the HO_x, NO_x and ClO_x reaction cycles. It considers the Chapman cycle, solves partial differential equations analytically, uses the Rosenbrock numerical method, discusses the trade-offs in the design of a kinetic model, and comments on photolysis in general.

   (g) [47] shows how lasers are used to study femtosecond reactions.

5. kinetic theory of gases
   (a) [3] and [23] discuss the Maxwell–Boltzman distribution of the velocities of molecules in a gas, using symbolic integration and differentiation.

6. reaction mechanisms and reactivity
   (a) [35] considers the reactivity of aromatic systems in relation to charge distributions computed theoretically by Hueckel theory.

7. crystallography
   (a) [22] discusses the analysis of the powder diffraction pattern of alkali crystal lattices.
   (b) [21] shows how to find whether a bromobenzoic acid crystal contains o-, m- or p- substituted molecules, and if hydrogen bonding is present.

8. infra-red spectroscopy
   (a) [25] discusses the vibrational energy levels of CO_2.
   (b) [49] discusses waveforms, resolution, spectral width and beat patterns.

9. UV–visible spectroscopy
   (a) [66] gives a self-contained discussion of Franck-Condon coefficients and gives data for the alkene double bond as an illustration.
   (b) [67] discusses the vibronic spectra of diatomic molecules and Birge–Sponer extrapolation. It shows how to explain the relationship between ground and excited state potential energy curves.
   (c) [36] discusses the iodine spectrum, using the principles that [66, 67] explain.

10. laser spectroscopy
    (a) [8] discusses femtosecond measurements. It introduces the time dependent Schrodinger equation and superposition of quantum states and it shows how to relate the pulse duration to ultrafast chemical reactions.
    (b) [47] shows how amplification by the active medium and the reflectivity of the cavity mirrors affects the laser power, considers the time dependence of the radiation in the laser cavity, and explains basic ideas of laser operation.

11. nuclear magnetic resonance
    (a) [48] discusses acquisition parameters, quadrature detection, apodization, zero filling, Fourier transforms, dwell time, aliasing and signal to noise ratio.

12. quantum theory

(a) [33] discusses the Bohr correspondence principle
(b) [43] discusses blackbody radiation
(c) [8] introduces the time dependent Schrodinger equation by reference to femtosecond chemistry.
(d) [7, 16, 33, 38, 46] discuss the energy levels of the particle in a box.
(e) [6, 7, 15, 24, 38, 40, 59, 61, 64] discuss the harmonic oscillator as a self-contained exercize or in the context of a more extensive problem.
(f) [15, 38] discuss the energy levels of a Morse oscillator.
(g) [25, 49, 50, 67] discuss vibrational energy levels of actual molecules in the context of infra–red spectroscopy (see above).
(h) [4, 9, 44] discuss formulas for atomic orbitals and the visualization of their charge distribution.
(i) [55] discusses bonding and antibonding orbitals by reference to the hydrogen molecule ion.
(j) [35] provides an extensive introduction to Huckel theory.
(k) [36, 66, 67] discuss electronic energy levels in a spectroscopic context (see above).
(l) [57, 62] provide short introductions to orthornormal functions and waves.
(m) [7] illustrates the combination of basis functions and the variational method.

13. Statistical methods in data analysis

    (a) [13, 18, 30, 32, 53, 51] discuss signals and noise, the propagation of error, Gaussian distributions, rejection of data, and linear and non–linear least–squares regression.
    (b) [41] considers damped oscillations to illustrate data–fitting.
    (c) [63] uses sum of squares deviations (SSD) and the F-test.

14. Other mathematical methods

    (a) [57, 60] introduce special functions of mathematical physics, in the form of Hermite polynomials.
    (b) [62] introduces wave motion.
    (c) [42] introduces matrix operations.
    (d) [7, 35] solve secular equations.
    (e) [15, 21, 49] explain and use Fourier series.
    (f) [27] deal with partial differential equations.
    (g) [37] discusses the method of steepest descents and [17] discusses congruent gradients for optimization.
    (h) [2, 5] describe Runge–Kutta integration of an ode.

References

[1] Bopp, A. F. A chemical kinetics application of MathCad.

[2] Coleman, F. Kinetics of complex reactions: steady–state and equilibrium approximations.

[3] Coleman, F. Maxwell–Boltzman distribution.

[4] Coleman, F. Radial distribution functions.

[5] Coleman, F. The steady–state and equilibrium approximations: background reading.

[6] Draves, J. A. Heat, work and entropy: a molecular level illustration.

[7] Dunn S. D. Variational method applied to the harmonic oscillator.

[8] Ellison, M. Femtosecond chemistry.

[9] Ellison, M. Orbital graphing.

[10] Ferguson, A. The Gibbs free energy of a chemical reaction system as a function of the extent of reaction and the prediction of spontaneity.

[11] Ferguson, A. Temperature as a measure of the distribution of particles over energy states: would a negative absolute temperature be very cold or very hot?

[12] Ferguson, A. Work done during reversible and irreversible isothermal expansion of a real gas.

[13] Fountain, A. W. Signals and noise.

[14] Garcia, J. A. C. ABC kinetics.

[15] Grubbs, W. T. Fourier transforms of molecular vibrations.

[16] Grubbs, W. T. Variational principles applied to the particle in the box.

[17] Hamilton, T. P. Optimization of geometries by energy minimization.

[18] Hansen, P. J. Introduction to the propagation of error.

[19] Hardgrove, G. Ideal gas law — introduction to MathCad.

[20] Hardgrove, G. Entropy of lead.

[21] Hardgrove, G. Crystal structure of bromobenzoic acid.

[22] Hardgrove, G. Powder pattern simulations.

[23] Hardgrove, G. Maxwell distribution of gas molecule velocities.

[24] Hardgrove, G. Vibrations of molecules I: the simple harmonic oscillator.

[25] Hardgrove, G. Vibrations of molecules II. the carbon dioxide molecule.

[26] Harris, H. The Carnot cycle.

[27] Harvey, E.; Sweeney, B. Modeling stratospheric ozon kinetics.

[28] Iannone, M. Fourier transform simulations.

[29] Krause, P. Enzyme activity as a function of pH.

[30] Lehmann, K. Gaussian distributions.

[31] Lehmann, K. Mean versus median.

[32] Lehmann, K. Rejection of data.

[33] Lo, G. V. Illustrating the Bohr correspondence principle.

[34] Lo, G. V. Relating qualitative analysis to equilibrium principles.

[35] LoBue, J. L. Huckel theory.

[36] Long, G.; Zielinski, T. J. The iodine spectrum.

[37] Madura, J. D.; Zielinski, T. J. Steepest descents: finding the minimum in a function

[38] Metz, R. Energies and wavefunctions for several one–dimensional potentials.

[39] Noggle, J. H. Computing a flame temperature.

[40] Pojman, J. A. Studying non–linear dynamics with numerical experiments.

[41] Poshusta, R. D. Data analysis (damped oscillations) using the sc genfit function.

[42] Reeves, M. S. Introduction to matrices: a tutorial for physical chemists.

[43] Shalhoub, G. M. Blackbody radiation.

[44] Shalhoub, G. M. Properties of the radial functions.

[45] Schwenz, R. W; Polik, W.; Young, S. Analysis of the vibrational spectrum of a linear molecule.

[46] Tisko, E. L. Visualizing particle-in-a-box wavefunction using MATHCAD.

[47] Vaksman, M. A. Exploring laser generation.

[48] Van Bramer, S. An introduction to NMR concepts.

[49] Van Bramer, S. Studies in FT–IR.

[50] Young, S. Computing a liquid–vapor phase diagram.

[51] Young, S. Non-linear least squares regression.

[52] Young, S. A summary of statistical thermodynamic calculations.

[53] Young, S.; Wierzbicki, A. Linear least squares regression.

[54] Young, S.; Zielinski, T. J. An introduction to MATHCAD.

[55] Zschocher, R.; Fowler, S. B.; Poler, J. C $H_2^{\pm}$ MO bonding and antibonding orbitals.

[56] Zielinski, T. J. Exploring the Morse potential.

[57] Zielinski, T. J. Exploring orthonormal functions.

[58] Zielinski, T. J. Fitting a polynomial to C_p *vs* T for Ag.

[59] Zielinski, T. J. Harmonic oscillator wave function explorations.

[60] Zielinski, T. J. Introductory explanation of the Fourier series.

[61] Zielinski, T. J. Modeling chemical bonds with a mathematical function.

[62] Zielinski, T. J. Playing with waves.

[63] Zielinski, T. J. van der Waals and Redlich–Kwong: fitting two-parameter equations to gas data

[64] Zielinski, T. J.; Miles, D. G. Numerical solution of second order differential equations.

[65] Zielinski, T. J.; Noggle, J. H. Real gases: defining the standard state and quantifying deviations from ideality.

[66] Zielinski, T. J.; Shalhoub, G. M. Introduction to Franck-Condon factors.

[67] Zielinski, T. J.; Shalhoub, G. M. Vibronic spectra of diatomic molecules and the Birge-Sponer extrapolation.