

The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed 14 double-spaced pages and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

INCORPORATION OF DATA ANALYSIS Throughout the ChE Curriculum MADE EASY WITH DATAFIT

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At Florida Tech, we have incorporated DataFit (from Oakdale Engineering^[1]) throughout the entire curriculum, beginning with ChE 1102, which is an eight-week, one-day-per-week, two-hour, one-credit-hour, second-semester Introduction to Chemical Engineering course in a hands-on computer classroom.^[2] Our experience is that students retain data analysis concepts when such concepts are formally taught to them in ChE 1102 and periodically reinforced throughout their academic careers. This paper outlines examples of several problems that have been included in my senior and graduate courses, including heat of absorption of hydrogen into a metal hydride, particle size distributions, and reaction rate law analysis. All Excel and DataFit files are available at:

<<http://my.fit.edu/~jbrenner/datafitanalysispaper2.zip>>.

THE HEAT OF ADSORPTION OF HYDROGEN ONTO A METAL HYDRIDE

It is rare for ChE students to learn much about gas/solid equilibrium, despite its importance in gas sensing, adsorption, chromatography, and catalysis. A relatively simple experiment to add to a unit operations laboratory that reinforces not only thermodynamics, but also dynamic mass and energy balances, is adsorption of hydrogen onto a metal hydride powder inside a hydrogen storage bed.

The following derivation begins with the thermodynamic relationships defining Gibbs free energy (ΔG) and the equi-

librium constant (K_{eq}), for the reaction of H_2 gas, at pressure P_{H_2} , with two vacant sites (whose concentration will be denoted as $[*]$) in the metal hydride to form surface-bound hydrogen (whose concentration will be denoted as $[H^*]$).

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_{eq} \quad (1)$$

$$K_{eq} = \frac{[H^*]^2}{P_{H_2} [*]^2} \quad (2)$$

The theoretical maximum hydrogen-to-metal (H/M) ratio is given in a crystal structure for the metal hydride: 1:1 for AB_5H_y (A and B are metals such as La and Ni; $y = 0-6$) hydrides. The maximum total site density for hydrogen storage, $[H/M]_{max}$, is the sum of vacant and hydrogen sites divided by the number of metal atoms in the metal hydride. If the activity coefficients are all unity, as would be the case if the gas phase and surface phase are ideal, one can substitute for the number



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of surface sites that hydrogen has adsorbed, $[H^*]$, and also apply some rules of logarithms to yield:

$$RT \ln P_{H_2} - 2RT \ln \left[\frac{H}{M} \right]_{\max} - [H^*] + 2RT \ln [H^*] = \Delta H - T\Delta S = \Delta G \quad (3)$$

If f_v is the fraction of vacant sites,

$$f_v = \frac{[H^*]}{\left[\frac{H}{M} \right]_{\max}} \quad (4)$$

Division of Eq. (3) by RT yields:

$$\ln P_{H_2} = \frac{\Delta H}{R} \left(\frac{1}{T} \right) - \frac{\Delta S}{R} + 2 \ln \left[\frac{H}{M} \right]_{\max} + 2 \ln(1 - f_v) - 2 \ln f_v \quad (5)$$

Nonideal gas and surface behavior will change the magnitude of the entropic term, but should not affect the enthalpic term.

It is common in hydrogen storage to plot the phase equilibrium relationships between hydrogen pressure in the gas phase (P) vs. the concentration of hydrogen in a metal hydride, usually expressed as either C for concentration or H/M atomic ratio for the hydrogen-to-metal ratio (the latter of which will be used here), at constant temperature (T). The adsorption isotherms shown in Figure 1 are for a proprietary $LaNi_{5-x}Al_x$ hydride whose metal alloy precursor was sold by Ergenics^[3] and converted into a hydride by myself and others.^[4] For the very common AB_5H_y -type hydrides ($y = 0$ to 6 , A and B are different metals), the maximum H/M atomic ratio is 1.0 .

Certainly DataFit is capable of fitting the phase equilibrium relationship for Figure 1, provided the user is capable of defining an appropriate model, but a model of this complexity is beyond the scope of this paper. It is conventional in the metal hydrides community to make what is known as a van't Hoff plot of the natural logarithm of hydrogen pressure as a function of reciprocal temperature at a fixed hydrogen content in the plateau region. It is common in $LaNi_{5-x}Al_x$ hydride literature to choose the H/M atomic ratio = 0.3 in order to construct this plot.^[4] For $LaNi_{5-x}Al_xH_y$ ($y = 0-6$) compounds, $[H/M]_{\max} \cong 1$. Thus, an H/M atomic ratio of 0.3 corresponds to $f_v = 0.3$. Thus, when one makes the van't Hoff plot using the data in `lani5.dft` (inside `<http://my.fit.edu/~jbrenner/datafitanalysispaper2.zip>`), the entropic term and those to the right of it in Eq. (5) equal the intercept of Figure 2, where the slope of Figure 2 is $\Delta H/R$. When one fits this data in DataFit, according to Eq. (6),

$$\ln P = Y = A - BX, \text{ where } X = \frac{1000}{T} \quad (6)$$

one finds the intercept is 20 ± 1 and the slope is -4.2 ± 0.5 , which gives an entropy of reaction of (-156 ± 11) kJ/K-mole and a heat of reaction of (-35 ± 4) kJ/mole.

PARTICLE SIZE DISTRIBUTION ANALYSIS

Students should have been exposed to both the probability density, $f(z)$, and cumulative density functions, $F(z)$, of the unit normal (or Gaussian) distribution in previous courses, where erf is the error function:

$$f(z) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{2}\right) \quad (7)$$

$$F(z) = \int_{-\infty}^z f(z) dz = 0.5 + 0.5 \operatorname{erf}\left[\frac{z}{\sqrt{2}}\right] \quad (8)$$

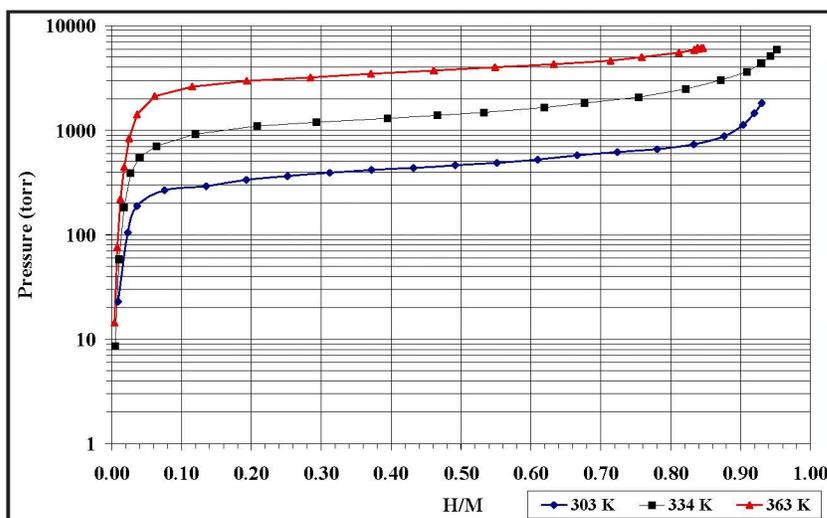


Figure 1. Equilibrium pressure vs. hydrogen content (H/M atomic ratio) plot, parametric in adsorption temperature for a $LaNi_{5-x}Al_x$ hydride^[4].

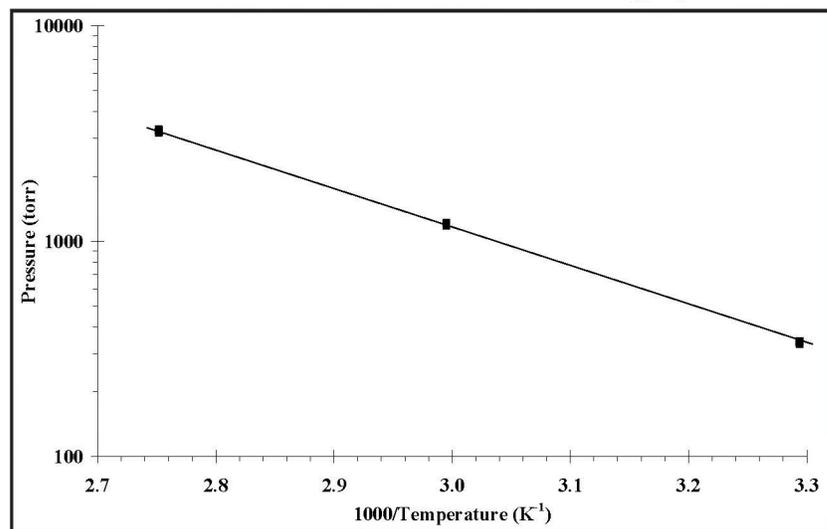


Figure 2. Van't Hoff plot for a $LaNi_{5-x}Al_x$ hydride at constant $H/M = 0.3$.

Based on coalescence theory, Granqvist and Buhman have shown that particle size distribution data should be approximated using log-normal distribution,^[5] which is similar to the normal distribution except that $z = (\ln d_i - \ln d) / \ln \sigma_d$ where d_i represents the particle diameter, d is the log mean particle diameter, and σ_d is the geometric standard deviation of diameters. Since the particle diameters are logarithmically distributed, evaluation of the standard deviation without using probits analysis is difficult. Probits analysis allows one to transform a Gaussian distribution into a straight line using the inverse normal distribution function. The first step in probits analysis is the definition of a geometric standard deviation (GSD). The GSD is the particle diameter greater than 84.13% of the particles in the distribution divided by the diameter greater than 50% of the particles. The particle size distribution data set in Figure 3 was obtained by Brenner et al.^[6] for a series of Fe nanoparticles prepared by microwave dissociation of neat $\text{Fe}(\text{CO})_5$ in Ar, and can be found in

fenosols03final.xls and probits.dft inside the aforementioned datafitanalysispaper2.zip.

The distribution is plotted as a probability density function, which is constructed in Excel as follows:

- 1) Determine the particle diameters for each particle, and enter them into column A in Excel.
- 2) Make a row across the top of the spreadsheet ranging from -1.0 to 2.0, in 0.1 increments, in cells B1 to AE1.
- 3) Define Eq. (9) in cell C2, where the "1" between the two commas is the "true" case of the logical test, and the "0" is the "false" case of the logical test.

$$= \text{IF}(\text{B}\$1 \leq \log(\$A2) \leq \text{C}\$1, 1, 0) \quad (9)$$

- 4) Copy and paste Eq. (9) in columns C through AE and from rows 2 down to the bottom of the data set. This operation groups the particle diameter into 30 logarithmically and evenly spaced bins ranging from 0.1 nm to 100 nm.

5) Sum each of the columns C through AE and divide each column by the total number of particles to get a probability density function.

6) Sum up the particle counts in each column to create a cumulative density function.

If one instead plotted the data as a cumulative distribution function, one would see a sigmoidal, or S-shaped curve. It is much easier to fit cumulative distribution functions than their derivatives, the probability density functions, as the latter have substantially higher errors. In order to plot such functions as straight lines unless one has a program capable of plotting data using probability axes (such as Kaleidagraph), the best way to analyze this kind of problem is using probits analysis, which requires the NORMINV function in Excel:

$$= \text{NORMINV}(C / 100, D, E) \quad (10)$$

where C is the cumulative percentage of particles with diameters less than "d," D is the number of probits at the mean (exactly 5 for 50%), and E is the number of probits corresponding to the standard deviation (set to 1). In theory, the number of probits should range from 0 to 10. Given that the error in the probability densities is about 0.5%, however, the practical linear range for the data in Figure 4 is between 2 and 8.

◀ **Figure 4.** Cumulative probability function plotted in probit form for particle size distribution of Fe nanoparticles prepared via microwave plasma dissociation of neat $\text{Fe}(\text{CO})_5$ in Ar.^[6]

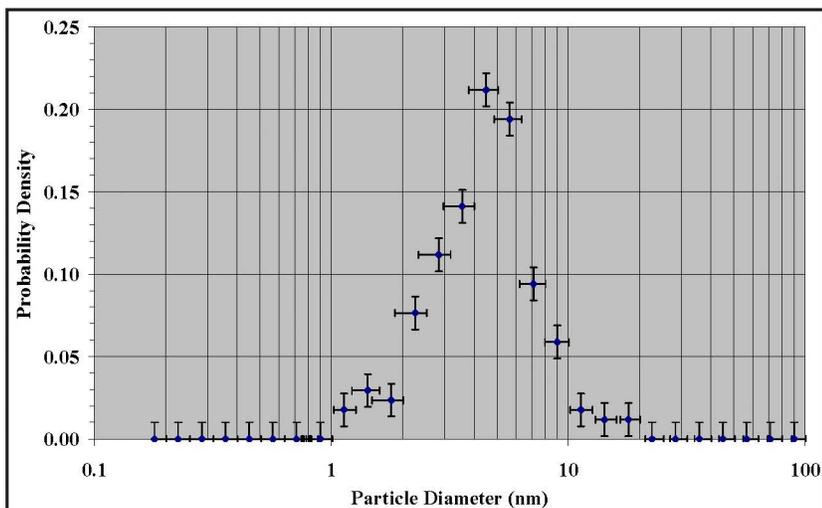
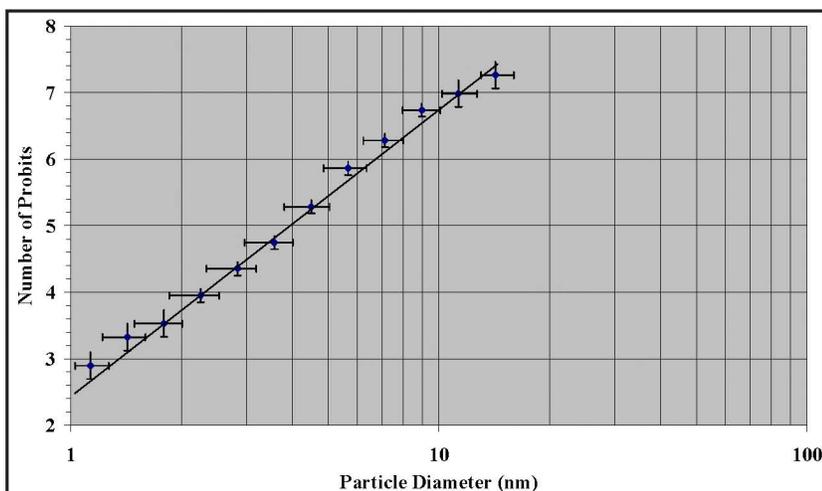


Figure 3. Probability density function for particle size distribution of Fe nanoparticles prepared via microwave plasma dissociation of neat $\text{Fe}(\text{CO})_5$ in Ar.^[6]



Graphically, the probit mean of 5 should correspond to the geometric mean of the particles (~ 4.0 nm), and the ratio of the diameter at 6 probits (~ 6.4 nm) to the diameter at 5 probits (~ 4.0 nm) should provide the geometric standard deviation of the data (6.4 nm/4.0 nm = ~ 1.6). If one takes the logarithm of the diameter data, puts it in the “x” column in DataFit, puts the number of probits in the “y” column, performs a simple $y = ax + b$ fit, and finally goes into the Evaluate tab under “Results Detailed,” one can evaluate the diameter—albeit with some effort—at 5 probits (3.8 nm) and 6 probits (6.6 nm), giving rise to a geometric standard deviation of 1.7.

REACTION KINETICS: DEHYDROGENATION OF METHYLCYCLOHEXANE TO FORM TOLUENE

An example of a more advanced problem that DataFit makes surprisingly easy is fitting of chemical reaction rate data. Data for the dehydrogenation of methylcyclohexane to form toluene over a 0.3 wt. % Pt/Al₂O₃ catalyst is cited in Problem 5.19 in Fogler’s reaction engineering textbook,^[7, 8] and in prob519b.dft. Fogler’s problem suggests four possible rate laws to use, where M denotes methylcyclohexane:

$$1) -r_M = kP_M^\alpha P_{H_2}^\beta \quad 2) -r_M = \frac{kP_M}{(1 + K_M P_M)}$$

$$3) -r_M = \frac{kP_M P_{H_2}}{(1 + K_M P_M)^2} \quad 4) -r_M = \frac{kP_M P_{H_2}}{(1 + K_M P_M + K_{H_2} P_{H_2})}$$

Though physical insight is not asked for in the problem statement, this problem provides a wonderful opportunity to relate abstract mathematical models to adsorption equilibria. Unless the values of α and β are combinations of 1 and 0, then rate law 1 is a purely empirical model. Rate law 1 also implies the adsorption of all reactants and products is relatively weak.

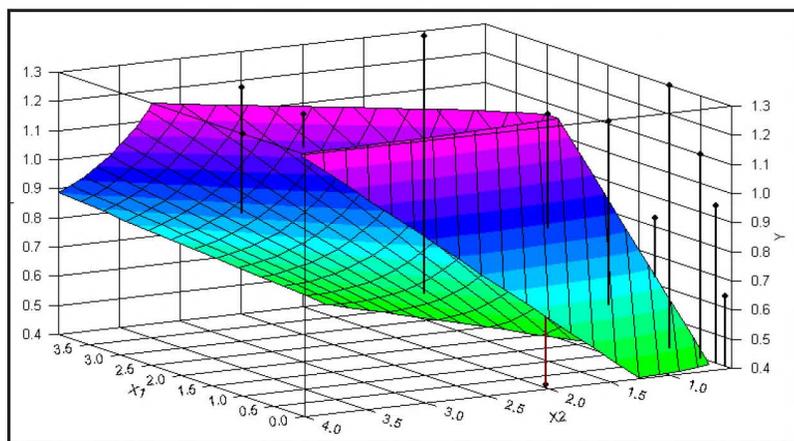
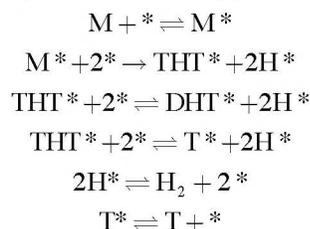


Figure 5. Although Model 3 was a successful fit according to DataFit, clearly the curve fit is not consistent with the data.^[7, 8] The vertical lines represent deviations between the experimental and calculated data.

The equilibrium constants in the denominators of rate laws 2, 3, and 4 must be positive, but some students will not recognize K_M or K_{H_2} as equilibrium constants and may have even forgotten what an equilibrium constant means. If THT denotes tetrahydrotoluene, DHT denotes dihydrotoluene, and * denotes a surface site, then Langmuir-Hinshelwood model 2 may be valid, given the following possible mechanism.



Model 2 describes a Langmuir dependence on methylcyclohexane only, and seems the most logical from a physical standpoint. The denominator in Model 2 is possible if the product of surface concentration and the equilibrium constant for adsorbed hydrogen is negligible compared with unity. If the reaction is surface reaction-limited, the rate-limiting step will be the initial dehydrogenation step because the increasing number of double bonds will allow the electrons to delocalize. LeChatelier’s principle leads us to believe that the rate of dehydrogenation should be favored by high methylcyclohexane pressures, and might be inhibited by both toluene and hydrogen. Rate laws 3 and 4 both have either a zero-order or first-order H_2 dependence.

What most students will not know until the faculty member discusses the homework solution is that, during dehydrogenation reactions, a parallel reaction typically occurs in which adsorbed toluene and/or partially hydrogenated intermediates are polymerized to form a carbonaceous overlayer known as coke. As this coke layer forms, the reaction rate will decrease. Usually, coke can be hydrogenated and then desorbed if not allowed to get very thick. As the coke layer gets thicker, it becomes very hydrogen-deficient and almost graphitic. With such insight into the catalytic chemistry, it becomes clear why a certain pressure of H_2 is necessary to prevent catalyst deactivation.

Lacking such physical insight, both undergraduate and graduate students consistently enter rate expressions into DataFit without much thought. Because Model 2 does not have a dependence on the hydrogen pressure, DataFit will balk until you supply a model definition that contains a 0^*X_2 , where X_2 is the hydrogen pressure. With that note, students should get the following results at the 95% confidence intervals (Table 1). The β parameter in Model 1 and all parameters in Models 3 and 4 are mathematically insignificant because the errors in these parameters are larger than the parameters themselves. Only Model 2 yields numbers that are mathematically significant. Of course,

Model #	k	K_M	K_{H_2}	α	β
1	1.1 ± 0.1	—	—	0.18 ± 0.09	-0.03 ± 0.13
2	12 ± 2	9 ± 3	—	—	—
3	3 ± 4	8 ± 19	—	—	—
4	$8 \times 10^{36} \pm 1 \times 10^{45}$	$7 \times 10^{36} \pm 9 \times 10^{44}$	$5 \times 10^{36} \pm 7 \times 10^{44}$	—	—

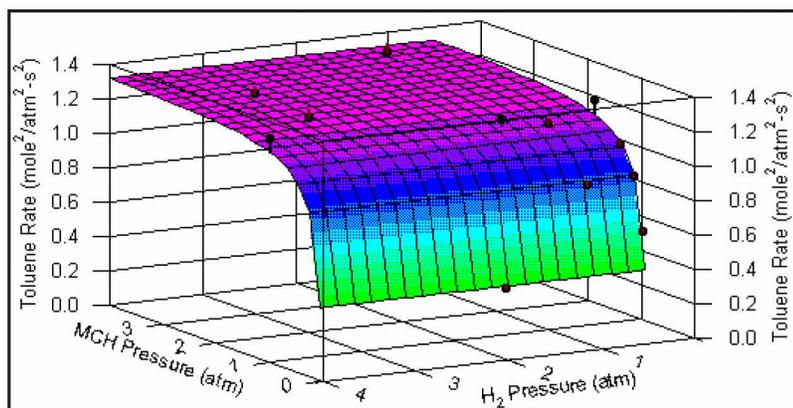


Figure 6. Langmuir dependence of toluene production rate on methylcyclohexane pressure without hydrogen dependence (Model 2).

that does not mean this is the best possible model, only the best of the four models in Professor Fogler's problem. It is important to point out that DataFit says all four curve fits were "successful," but Figure 5 (for Model 3) clearly demonstrates that a successful fit may mean absolutely nothing.

The default DataFit plot for 3-D plots such as Figure 5 are colorful, but would be far superior if proper labels were applied. By clicking the Format button and applying some format options, one can obtain a plot similar to Figure 6 for Model 2. For 2-D plots, I would not ask students to spend time modifying plot scales, labels, etc., because plots are far easier to make in Excel and are of a higher quality. Excel, however is sorely lacking when it comes to 3-D plots, forcing people to use what Microsoft calls category axes—thus restricting 3-D plots in Excel to bar charts.

CONCLUSIONS

The reason that I downloaded DataFit in the first place was not because of its excellent curve-fitting capabilities, but

because—as of 1998 when I first started using it while in industry—DataFit was the only program that did proper 3-D scientific plotting for less than \$500. In 1999, when Florida Tech bought a site license for DataFit version 6.1, it cost only \$750 for the entire campus (albeit a relatively small campus), whereas a single copy cost \$100. Moreover, the site license allowed students and faculty to use DataFit at home as long as they were doing academic work.

As reported in a companion paper,^[2] 11 of 12 international graduate students without previous exposure to either Polymath or DataFit found fitting of vapor pressure data to be easier using DataFit. Of the first 20 undergraduates who were exposed to DataFit for four years, all rated it as "excellent" or "above average" in exit surveys. Students throughout Florida Tech's College of Engineering have also awarded me consecutive student-nominated, college-wide teaching awards. I attribute this success largely to consistent reinforcement of data analysis skills.

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