Mathematica-Assisted Learning in Physical Chemistry

R. W. Kaziro

Department of Chemistry, Faculty of Informatics, Science and Technology, University of Western Sydney, Macarthur, P.O. Box 555, New South Wales, Campbelltown 2560, Australia

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Mathematica is a general software system for mathematical applications. It is now being used by physical chemistry students at the University of Western Sydney, Macarthur. *Mathematica* has assisted students in concentrating on learning physical principles and analyzing experimental data. According to the students, the program provided them with a means of quickly solving numerical problems. Nonetheless, students experienced difficulties due to language and syntax of *Mathematica*. Subsequently, the data entry and word processing systems have been simplified by providing the students with standard *Mathematica* packages in which they typed the appropriate expressions to fit their results and plot the graphs.

INTRODUCTION

Mathematica[1] was introduced in the B.Sc. course in an effort to encourage undergraduate students overcome common obstacles in learning physical chemistry. Often students spend more time on the mathematical aspect of analyzing experimental data rather than concentrating on learning physical principles. In particular, most students find kinetics, thermodynamics, and quantum chemistry extremely mathematically demanding. In addition to the difficulties experienced in the process of learning physical chemistry, the assessment of advanced physical chemistry is dominated by algebraic manipulations and numerical problems. Most students pursuing chemistry are disadvantaged if they find it difficult to reach the required mathematical level.

Mathematica is perceived to be a suitable tool for calculating numerical results both from theoretical examples and from real experimental data. In essence *Mathematica* consists of hundreds of built-in mathematical functions for the completion of calculations and the presentation of graphics. *Mathematica* performs fast and accurate symbolic calculations and creates both visualization and sound to match various functions and data. Due to its enhanced capacity in word processing (and not withstanding its cost), *Mathematica* supersedes a normal calculator that can only be used for numerical calculations.

Although *Mathematica* is a major advance in the technology of mathematics, the critical factor is the students' ability to use and adapt it to problem solving. The prime objective in the teaching of problem solving in physical chemistry, unlike mathematics, is to engage the students in the actual subject matter. The desired strategy is to improve the students' understanding of the basic concepts and their applications to problems in the real world. For this reason, the intention behind using *Mathematica* was not just to replace symbols in a given equation and find a numerical solution but to enable the students to concentrate on the content of a problem and to select the appropriate expression for problem solving.

This paper examines the students' orientations toward studying Physical Chemistry via *Mathematica*. It identifies three stable orientations or styles in learning as previously described by Entwistle and Ramsden.[2] The students can adopt "Reproducing Orientation", if they have a sense of extrinsic motivation, fear of failure and anxiety, and syllabus boundedness. Thus, they adopt a "Surface Approach" to learning.[3] The students can adopt a "Personal Meaning Orientation" which is associated with intrinsic motivation, a preference for autonomy, and a "Deep Approach" to learning.[3] The students can also adopt a middle style called "Achieving Orientation" and associated with "Strategic Approach" to learning.[4] The orientations are examined by psychometric methods involving questionnaires,[2] while the approaches are obtained by a phenomenographic perspective, which is based on interviewing the students.[3,5] However, the two perspectives reach similar conclusions concerning student learning.

Despite its use as a learning tool, computer-assisted learning can tend to encourage superficial learning approaches in students. Superficial learning is associated with the students' "Surface Approach" of learning, which is interpreted as the "Reproducing Orientation". The use of *Mathematica* was intended to discourage such superficial learning outcomes.

Students initially typed their own packages, but they encountered problems centering on the syntax of *Mathematica*. To overcome the problems, the students were provided with *Mathematica* packages in which they were expected to type the appropriate expressions to fit their results and plot the graphs. The packages were specifically designed to provide guidance in these areas. A similar approach was previously adopted with *Mathematica* for determining chemical solubilities of salts.[6]

Further research examined the students' own evaluation of the learning outcomes from *Mathematica*. A questionnaire, modified from an original instrument by Ernest, McDonald, and Moses,[7] was administered to second year undergraduates in June of 1995, 1996, and 1997 after their use of *Mathematica*. This ascertained how they perceived their own

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Linear and Nonlinearfit Package

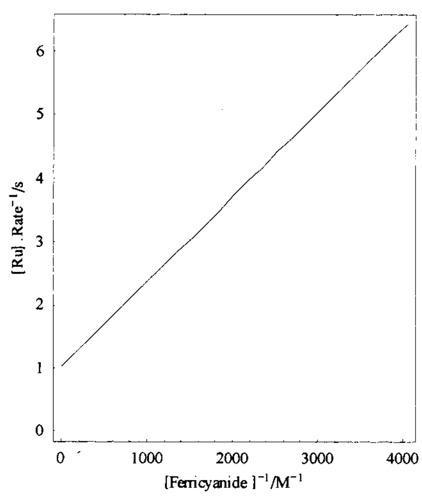
```
<< "Statistics`NonlinearFit`"

pa = {{0.007, 0.90}, {0.005, 0.82}, {0.004, 0.71}, {0.002, 0.63},
{0.001, 0.39}, {0.00075, 0.35}, {0.0005, 0.26}, {0.00025, 0.16}};
ALC := 0.025
```

Linearfit

```
pg[{x_, y_}] := {1/x, 1/y}

ng = pg/@ pa

{{142.857, 1.11111}, {200., 1.21951}, {250., 1.40845}, {500., 1.5873}, {1000., 2.5641}, {1333.33, 2.85714},
 {2000., 3.84615}, {4000., 6.25}}

Fit[ng, {1, x}, x]

1.03484 + 0.00133299 x

tr = Plot[%, {x, 0, 4050}, PlotStyle → PointSize[.03], DisplayFunction -> Identity]

- Graphics -

mp = ListPlot[ng, DisplayFunction -> Identity]

- Graphics -
```

This plots the points and the line of best fit.

```
Show[mp, tr, DefaultFont → {"Times", 10},
FrameLabel -> {"[Ferricyanide]^-1/M^-1", "[Ru].Rate^-1/s"}, AxesOrigin → {0, 0},
AspectRatio → 1.18, Frame → True,
ImageSize -> 300, FrameTicks → {Automatic, Automatic, None, None},
DisplayFunction -> $DisplayFunction];
```



Nonlinearfit

NonlinearFit$\left[\text{pa}, \dfrac{2\,\text{a}\,\text{bALC}\,\text{x}}{2\,\text{a}\,\text{ALC} + \text{bx}}, \{\text{x}\}, \{\text{a}, \text{b}\},\right.$

MaxIterations → 999, Method → FindMinimum, PrecisionGoal → 99999, AccuracyGoal → 99999$\left.\right]$

$$\frac{721.981\,x}{1.07258 + 673.124\,x}$$

```
lp := ListPlot[pa, PlotStyle → PointSize[0.02], ImageSize -> 300,
   PlotRange → {0, 1.00}, DisplayFunction -> Identity];

ls := Plot[721.981474885552199` x / (1.07258391019427823` + 673.123536558346291` x), {x, 0, 70.5/10^4},
 ImageSize -> 200, PlotStyle → PointSize[.01], DisplayFunction -> Identity]

Show[{ls, lp}, DefaultFont → {"Times", 10},
FrameLabel → {"[Ferricyanide]/M", "Rate.[Ru]^-1/s^-1 "}, AxesOrigin → {0, 0},
AspectRatio → 1.18, Frame → True, ImageSize -> 300,
FrameTicks → {Automatic, Automatic, None, None}, DisplayFunction -> $DisplayFunction];
```

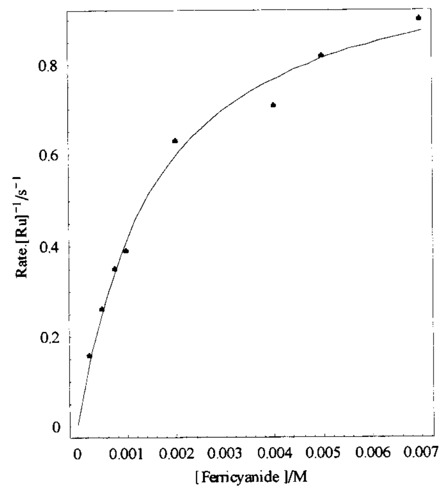


Figure 1. Nonlinear plot.

learning outcomes in physical chemistry. The students' experiences revealed that *Mathematica* had assisted them in concentrating on learning physical principles and analyzing experimental data. In addition, *Mathematica* provided an easy means of quickly solving numerical problems.

METHODS, STRATEGIES, AND ACTIVITIES

The implementation of the project depended on the two *Mathematica Version 2.2.3* systems, which were later upgraded to *Version 3.0*. They were purchased from Wolfram Research and installed independently on two computers donated by the Chemistry Department. Within limitations of the license and computers, the students were taught individually or in pairs. The pilot training began in the middle of the Autumn semester in 1995 with 20 students. Individual students participated in using *Mathematica* for the following activities: (a) linear and nonlinear plot of best fit and graphical presentation of experimental results; (b) experimental data analyses; (c) numerical and symbolic calculations of problems and exercises from the physical chemistry textbook(s)[8,9] laboratory manual and assignments;[10] and (d) the word processing of reports.

The subsequent program was implemented in the autumn semesters of 1996 and 1997 with 30 second year physical chemistry students. In order to compute kinetics constants, present graphics of a linear and nonlinear plots of best fit, and solve physical chemistry problems, the students were provided with *Mathematica* packages,[1,11] as illustrated in the screen prints. These are attached after obtaining permission from *Mathematica* Research, Inc. as shown in Figures 1−3.

The students typed their experimental data in the package and changed the range of the *Y*-axis variable and the axes-labels according to the size and nature of the measurements. The *Mathematica* program converted the data for a double reciprocal plot and gave an equation and a graph for a linear fit to the new data. Figure 1 illustrates how the *Mathematica* program fitted points using a linear and nonlinear regression, a process which took only a few seconds.

Figure 2 illustrates a kinetics problem as it was solved by the students with the linear *Mathematica* package. To determine the kinetics for the conversion of ammonium cyanate into urea, $NH_4CNO \rightarrow NH_2CONH_2$, the students simply plotted two graphs. Since the second graph (example 2b) gave a better fit to the data than the first graph (example 2a), the reaction is first order in the concentration of urea. The slope gave the rate constant, $k = 0.0597\ M^{-1}\ min^{-1}$.

Figure 3 illustrates two physical chemistry problems as they were solved by the students using the command [Solve]. The vapor pressure was simply calculated from an equation of state, the van der Waals equation (example 3a). Thus the students were able to spend more time on discussing the reasons for deviation from the results obtained by means of the ideal gas equation (example 3b). A more tedious calculation of volume from the van der Waals equation expressed in the cubic form was also simply solved by using the *Mathematica* command [Solve] (example 3c).

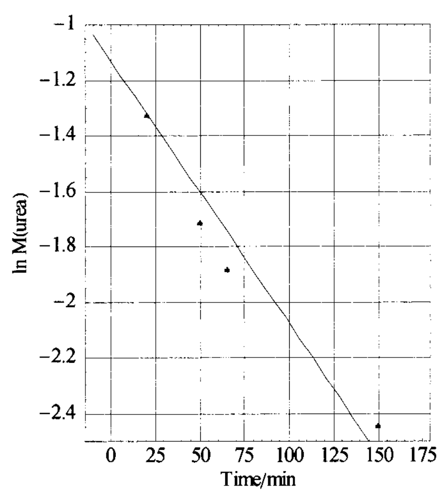
The students also completed the "Approaches to Studying Questionnaire".[12] This was intended to monitor the changes in the quality of learning in physical chemistry. As described by Gibbs,[12] the questionnaire consists of 18 items classified into three orientations: "Achieving, Reproducing, and Meaning". In the autumn semester of 1977 the students completed the questionnaires once before and after using *Mathematica*. The questionnaire was adapted as previously described by

Example 2 a examines first – order kinetics :

```
pr = Plot[%, {x, -10, 175}, PlotRange → {-2.5, -1.0}, Frame → True,
    GridLines → Automatic, PlotStyle → PointSize[.02],
    FrameLabel → {Time/min, ln M(urea)}, DisplayFunction → Identity]

- Graphics -

    kp = ListPlot[lt, DefaultFont -> {Times, 12}, PlotRange → {-2.5, -1.0},
    Frame → True, GridLines → Automatic,
    PlotStyle → PointSize[.02], AspectRatio → 1.2, ImageSize -> 300,
    FrameLabel → {Time/min, ln M(urea)}, DisplayFunction → Identity]

- Graphics -
```

This plots and joins the points of the line of best fit.

```
Show[kp, pr, DisplayFunction → $DisplayFunction];
```



This is the regression for fitting the model y = mx + b

```
<< Statistics`LinearRegression`
Regress[lt, {1, x}, x]
```

{ParameterTable →

	Estimate	SE	TStat	PValue
1	-1.12968	0.102362	-11.0361	0.00159342,
x	-0.00945396	0.00132983	-7.10918	0.0057268

RSquared → 0.943968, AdjustedRSquared → 0.92529,
EstimatedVariance → 0.0236617, ANOVATable →

	DF	SumOfSq	MeanSq	FRatio	PValue
Model	1	1.19587	1.19587	50.5404	0.00572
Error	3	0.070985	0.0236617		
Total	4	1.26685			

}

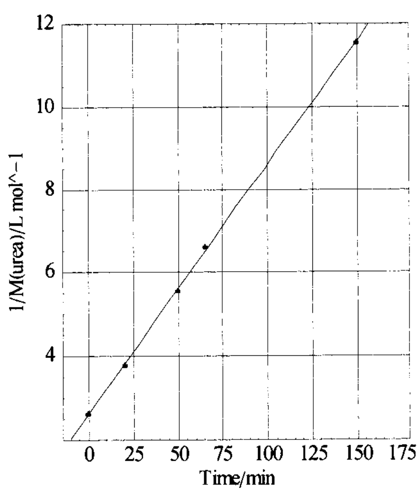
Example 2 b examines second – order kinetics :

$$\mathrm{sg}[\{x\_, y\_\}] := \left\{x, \frac{1}{\frac{22.9-y}{60.06}}\right\}$$

```
lg = sg/@ccl

{{0, 2.62271}, {20., 3.77736}, {50., 5.56111}, {65., 6.6},
 {150, 11.55}}

Fit[lg, {1, x}, x]

2.61942 + 0.0596985 x

sr = Plot[%, {x, -10, 175}, PlotRange → {2, 12}, Frame → True,
    GridLines → Automatic, PlotStyle → PointSize[.02],
    DisplayFunction → Identity,
    FrameLabel → {Time/min, 1/M(urea)/ L mol^-1}]

- Graphics -

kp = ListPlot[lg, DefaultFont -> {Times, 12}, PlotRange → {2, 12},
    Frame → True, AspectRatio → 1.2,
    ImageSize -> 300, GridLines → Automatic,
    PlotStyle → PointSize[.02], DisplayFunction → Identity,
    FrameLabel → {Time/min, 1/M(urea)/L mol^-1}]

- Graphics -
```

This plots and joins the points of the line of best fit.

```
Show[kp, sr, DisplayFunction → $DisplayFunction]
```




```
- Graphics -
```

This is the regression for fitting the model y = mx + b

```
<< Statistics`LinearRegression`
Regress[lg, {1, x}, x]

{ParameterTable →
        Estimate     SE             TStat      PValue
  1     2.61942      0.0451317      58.0395    0.0000112677
  x     0.0596985    0.000586324    101.818    2.08854 × 10^-6

 ,
 RSquared → 0.999711, AdjustedRSquared → 0.999614,
```

Figure 2. Analyzing kinetics data.

Gibbs,[12] and the students' scores are discussed in the Outcomes section of this paper.

After the use of *Mathematica* in Physical Chemistry for first semester in 1996 and 1997, the students also completed

Example 3 *a*

Type input data:

```
T := (273 + 120) K
V := 32.50 L
a := 5.463 (L^2 atm) / mol^2
b := 0.03049 L / mol
R := 0.08206 (L atm) / (K mol)
n := 1.0 mol
```

Caculation of vapour pressure from a cubic equation of state, e.g. van der Waals equation:

```
Solve[x == ((n R T) / (V - n b)) - (a n^2) / V^2, x]

{{x → 0.988054 atm}}
```

Example 3 *b*

Calculation of vapour pressure from an ideal equation of state:

```
Solve[x == n R T / V, x]

{{x → 0.992295 atm}}
```

Example 3 *c*

Type Input data:

$$n := \frac{132\,\mathrm{mol}}{44.01}$$

$$P := 10.0\,\mathrm{atm}$$

$$T := 280\,\mathrm{K}$$

$$a := \frac{3.59\,\mathrm{dm}^6\,\mathrm{atm}}{\mathrm{mol}^2}$$

$$b := \frac{0.0427\,\mathrm{dm}^3}{\mathrm{mol}}$$

$$R := \frac{0.0825\,\mathrm{dm}^3\,\mathrm{atm}}{\mathrm{K\,mol}}$$

Calculation of volume from a cubic equation of state, e.g. van der Waals equation:

$$\mathrm{Solve}\left[x^3 - \frac{(n\,x^2)\,(R\,T + b\,P)}{P} + \frac{x\,(n^2\,a)}{P} - \frac{n^3\,a\,b}{P} == 0,\ x\right]$$

$$\{\{x \to (0.240813 - 0.07012\,I)\,\mathrm{dm}^3\},\ \{x \to (0.240813 + 0.07012\,I)\,\mathrm{dm}^3\},\ \{x \to 6.57487\,\mathrm{dm}^3\}\}$$

Figure 3. Using the command [Solve] for solving equations of state.

Table 1. The Scores for the Four Students to the "Approaches to Studying Questionnaire" [a]

student	achieving orientation	reproducing orientation	meaning orientation
A	24	15	20
B	18	18	19
C	18	13	14
D	18	20	19
mean	19.5	16.5	18

[a] Each score is out of 24.

a questionnaire affording a self-evaluation of their learning outcomes from *Mathematica*. The questionnaire[7] consists of 18 items related to the students' knowledge, cognitive skills, experimental skills, and attitudes. Each item can be scored at five different levels ranging from the response that the student "definitely agrees" through to "definitely disagrees" with the statement. The probability (relative frequency) of each score is expressed as a percentage of the total scores.

OUTCOMES

The second year chemistry students who used *Mathematica* in 1995 made the following comments which proved valuable in confirming that computer support had a high potential in the students' learning.

Computers featured prominently in the presentation of results in the form of tables and groups.

Our teacher encouraged us to learn all the aspects of physical chemistry as well as the new computer program about *Mathematica*.

Get students to tabulate and specify the results of the prac in the report. It saves time and trouble, I think.

There was real enthusiasm shown by the teacher in applying computer-aids to make the students' tasks easier

At the end of the autumn semester in 1996, four second year chemistry students completed the "Approaches to Studying Questionnaire". Table 1 shows their scores.

The means of the students' scores (Table 1) show that the students score better in the "Achieving and Meaning Orientation" than in the "Reproducing Orientation". The mean scores are highest on the "Achieving Orientation" toward studying, which can be interpreted to mean that the students' learning is most influenced by the students' sense of competition for high grades. The students' score averages came up close second on the "Meaning Orientation" toward studying. It seems that the students have an intention to understand and maintain the structure of the task".[4] By contrast, the students scored lowest on the "Reproducing Orientation", which implies that their intentions are not simply "to complete and distort the structure of a task".[4] The students' mean scores were higher than those previously reported by Gibbs[12] for "Achieving, Reproducing, and Meaning Orientations" (Gibbs' figures were 13.08, 14.26, and 13.93, respectively. However, physical chemistry preliminary results, based on four students, are indicators of the students' good quality of learning. It may be noted that scores based on the small group sizes of students undertaking physical chemistry may not make the evaluations statistically significant, but the evidence of the programs could prove valuable.

In the autumn semester of 1996, 11 second year chemistry students completed the questionnaire on their experiences in using *Mathematica*. Their responses were analyzed by means of percentage frequencies for particular questions. At least 9% of the students "definitely agreed", but 45% "agreed with some reservations" that *Mathematica* had increased their knowledge. Their reservations may be attributed to the difficulties which the students expressed regarding the syntax of *Mathematica*. In addition, 27% of the students "strongly agreed" that the initial difficulties with the computer input using *Mathematica* discouraged them from using the software.

Similarly, 9% of the students "definitely agreed", while 36% "agreed with reservations" that *Mathematica* had improved their cognitive ability to think in abstract terms, logically, and independently. In addition, the students agreed by over 54% that *Mathematica* had improved their ability to apply new approaches to solve a new problem. Over 18% of the students "definitely agreed" that *Mathematica* has improved their experimental skills, but 36% "agreed with some reservations" that computers had improved their ability to make careful observations and interpret experimental results. The students' positive attitudes toward undertaking research, working with peers, and experiencing a sense of increased motivation was approximately 54%.

Preliminary results in 1995 and 1996 proved encouraging, and further research examined the students' approaches to learning at both the beginning and end of the 1997 autumn semester, again based upon their experiences of using *Mathematica*.

At the beginning of the 1997 autumn semester, thirteen second year students completed the "Approaches to Studying" Questionnaire. Mean scores for the students' "Achieving, Reproducing, and Meaning Orientations" were 16.2, 16.5, and 14.9, respectively. In the event, the students' "Meaning Orientation" score was the lowest, while the "Achieving and the Reproducing Orientations" were almost equally greater. At the end of the 1997 autumn semester, 23 second year students, after completing a *Mathematica* program, completed the "Approaches to Studying" Questionnaire. Their mean scores for the "Achieving, Reproducing, and Meaning Orientations" were 15.9, 15.8, and 16.0, respectively.

In the autumn semester of 1997, 17 second year chemistry students completed the questionnaire on their experiences in using *Mathematica*. The majority agreed that *Mathematica* had increased their knowledge, cognitive ability, experimental, and group-work skills in their understanding the physical principles. The number of students who "definitely agreed" on improvement of learning physical principles was over 200% greater in 1997 than that in 1996. This improvement may be attributed to the decision to provide the students with standard *Mathematica* packages in which they typed the appropriate expressions to fit their results and plot the graphs. Thus, data entry and word processing were simplified.

CONCLUSION

There was an apparent increase in the students' quality of learning Physical Chemistry after using *Mathematica*. The students' scores for the "Meaning Orientations" increased, but those for the "Achieving and Reproducing Orientations" decreased. The 1997 results monitored the students' orientations toward studying once before and once after using *Mathematica* for 12 weeks. The results obtained in the autumn semester in 1997 validate those obtained in 1996, where students were monitored once only at the end of the semester.

Based on the evidence of the students' experience, *Mathematica* has assisted students in concentrating on the learning of physical chemistry. Although *Mathematica* provides an easy means of quickly solving numerical problems, analyzing data and presenting graphics, at first, students did experience difficulties concerned with the syntax of *Mathematica*. However, the students overcame these difficulties by using *Mathematica* packages. Future research would examine the effect of *Mathematica* in order to test the extent of any correlation between the students' learning outcomes and the students' assessment results.

ACKNOWLEDGMENT

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