

XSEOS – an Open Software for Chemical Engineering Thermodynamics

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Abstract

An Excel[®] add-in – XSEOS – that implements several excess Gibbs free energy models and equations of state has been developed for educational use. Several traditional and modern thermodynamic models are available in the package with a user-friendly interface. XSEOS has open code, is freely available, and should be useful for instructors and students of chemical engineering thermodynamics courses.

Keywords: phase equilibrium; chemical equilibrium; equations of state; excess Gibbs free energy.

1. Introduction

Before computers, predictions of physical properties relied on graphical methods, correlations, and simple analytical models. Advances in molecular thermodynamics, statistical mechanics, and computer technology have changed this scenario forever. Thermodynamic models that take many details at molecular level into account are now available for several types of mixtures. Complexity usually prevents full derivations of these models in undergraduate classrooms, but it is possible to sketch their major assumptions and to discuss how they translate into model

capabilities and limitations. With this sort of background, students can apply these models to solve interesting computer-based chemical engineering thermodynamics problems.

There are different approaches to using these models in undergraduate courses. A possibility is to ask students to program the models they need, requiring many hours of development and debugging. Another approach is to use professional software such as ASPEN, HYSYS, or Simulis Thermodynamics, in which students select the components, physical property package, and type of calculation, and get results immediately. They may be left, however, with little understanding of the steps involved in a phase or chemical equilibrium calculation and there is little or no access to the code, frustrating curious students. An intermediate approach is to use open software for use in software like Matlab[®], Mathcad[®] or Excel[®], relieving students from the burden of writing long programs, yet enabling them to recombine parts of the code into new applications.

Many recent editions of textbooks on chemical engineering thermodynamics and related subjects provide computer programs as supplementary material (e.g., Smith et al. [1], Sandler [2], Elliot and Lira [3], Koretsky [4], Kyle [5], Cutlip and Shacham [6]). These programs often run in professional software such as Matlab[®], Mathcad[®] or Excel[®], or as stand-alone software, such as the well-designed ThermoSolver [7] package that accompanies Koretsky's book [4]. Another stand-alone software freely available is the VLE-Java program [8], which performs phase equilibrium calculations for binary mixtures using five different thermodynamic models.

An additional aspect, not to be neglected, is cost. Educational versions of professional software are available and affordable to many institutions and/or individuals, but this is not always the case, especially in developing countries. Availability and ease of use have made Excel[®] one of the platforms of choice for educational engineering software and, for example, its use for teaching chemical process design and integration has been recently discussed [9]. Actually, Excel[®] allows different levels of programming. Developers can implement their models

in Visual Basic for Applications (VBA) as functions that users can easily call from the spreadsheet. For example, long calculations such as those of activity and fugacity coefficients and residual and excess properties can be programmed in VBA and made available as spreadsheet functions that students can use to develop procedures for calculations such as bubble and dew points and flashes, without extensive knowledge of programming languages.

Elliot and Lira [3] followed this type of approach and developed excellent Excel[®] spreadsheets freely available in the Internet. Some of the newest models, however, are not available yet in their spreadsheets. Another limitation is that some of the models are implemented for binary mixtures only or for mixtures with up to five components. Therefore, even though the Elliot and Lira spreadsheets are an outstanding educational tool, improvements are possible.

This work presents a new computational package, XSEOS, primarily intended for use in undergraduate courses, but which may also be useful for graduate courses and research. XSEOS – Excess Gibbs Free Energy Models and Equations of State – is a freely available program with many traditional and modern thermodynamic models. Moreover, XSEOS is an expandable platform, with open source code, that will hopefully contribute to the exchange of experiences in the teaching of chemical engineering thermodynamics.

2. XSEOS

The underlying concept in XSEOS is that students should have easy access to calculations using modern thermodynamic models, to become aware of their existence and learn how to use them. The calculation experience, however, should not be limited to getting results from ready-to-use programs. Instead, students should engage in developing calculation procedures but not in long program development. For example, students can implement a bubble point algorithm in an Excel[®] spreadsheet but use the functions available in XSEOS to compute the activity or fugacity

coefficients required by their calculations. The XSEOS add-in does not contain ready-to-use VBA procedures for chemical equilibrium, flash, dew, and bubble point calculations - XSEOS provides the physical properties required by these calculations. Furthermore, the XSEOS add-in does not contain VBA functions for ideal gas and ideal solution properties, as it is simple to program them in a spreadsheet, and their implementation is a good exercise for students.

One of the major goals of XSEOS is to provide an environment where students can rapidly develop and test calculation procedures and compare the results of different models. Because ease of use was the major goal, the computer codes are not as efficient as they could have been if execution speed was the top priority. Nonetheless, speed of execution was never a limitation when XSEOS was tested in undergraduate and graduate courses at the United Arab Emirates University (UAEU), where students used the package in laptop computers to solve classroom and homework problems and to develop course projects.

Table 1 presents the models and properties currently available in the program. In all cases, with exception of the Margules model, users can perform calculations with any number of components, only constrained by the Excel[®], operating system, and computer limits. The core procedures for all thermodynamic models were automatically written in VBA using Thermath [10], a program for the implementation of thermodynamics models, based on Mathematica[®]. They essentially implement formulas for many physical properties derived from a given thermodynamic model. The procedures that implement equations of state also need a root-finding numerical method to determine molar volumes in the liquid or vapor phases: the Toplis et al. [11] method was used because it is applicable to cubic and non-cubic equations of state. These procedures are not used directly from the spreadsheet, as front-end procedures with more user-friendly calling protocols have been developed manually. The manual distributed with the program lists the procedures and explains how to use them.

3. Sample Calculations

This section presents two sample calculations. In the figures that support this discussion, cell formats are simple. The sample spreadsheet distributed with XSEOS uses colors consistently to indicate cells with specified and calculated values.

3.1 Bubble pressures of the mixture methanol(1) + water(2) at 333.15 K.

The objective of this example is to compute the bubble pressure of the mixture methanol(1) + water(2) at 333.15 K for several liquid phase compositions. Assuming ideal gas phase behavior, neglecting the Poynting correction and the fugacity coefficient at saturation, the total pressure (P) is given by:

$$P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat} \quad (1)$$

where x_i , γ_i , and P_i^{sat} represent the mole fraction, activity coefficient, and vapor pressure of component i . Activity coefficients will be calculated using the UNIQUAC model. Figure 1(a) shows the spreadsheet before the beginning of calculations, with entries for the universal gas constant (in J/mol), temperature, vapor pressures of methanol and water, and UNIQUAC r , q , and binary interaction parameters (a_{ij}). Cell C10, which represents x_2 , is programmed as 1-B10 (i.e., $1-x_1$) and, whenever the value of x_1 changes, the corresponding x_2 value is automatically recomputed. XSEOS has a function named `uniquac` that takes the universal gas constant, temperature, mole fractions, and UNIQUAC parameters as inputs to compute the logarithms of activity coefficients as outputs. This function, as well as many others in XSEOS, returns more than one output value. Functions of this type in Excel[®] are called array functions. To use an array function, the user *must mark* the empty spreadsheet cells that will receive the output *before* typing the function call. In Fig. 1(b), cells D10 and E10 are marked to receive the values of $\ln \gamma_1$ and $\ln \gamma_2$, and the function call is in preparation. In Fig. 1(c) the calling statement of function `uniquac`

is ready but has not been executed yet. Execution occurs by pressing the keys CTRL+SHIFT+ENTER simultaneously. Figure 1(d) shows the results of this action and Fig. 1(e) shows the set of results for the row. In this figure, cells F10 and G10 were calculated by taking the exponential of cells D10 and E10, cell H10 implements Eq. (1), and cells I10 and J10 implement:

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \quad (2)$$

Having computed the results for the first liquid phase composition, it is simple to compute for a series of compositions. The value of cell B11 in Fig. 1(f) (the value of x_1 in the second point of the composition series) is defined as the value of cell B10 (the value of x_1 in the first point of the composition series) plus a step size, taken here as 0.25. One can then mark cells C10 to J10 and drag the Fill Handle (the small black square that appears in the bottom right corner of the marked region) to row 11. All the values, from x_2 to y_2 are automatically recalculated. By now marking cells B11 to J11 and dragging the Fill Handle to lower rows, results from x_1 to y_2 for additional compositions are computed. Figure 1(f) shows the results of these operations that can be used, for example, to prepare a Pxy diagram using the plotting facilities available in Excel[®].

3.2 Flash calculation by direct minimization of the Gibbs function.

Minimization of the Gibbs function for a system with specified values of temperature, pressure, and initial amounts of each component is a fundamental criterion for thermodynamic equilibrium. In most undergraduate textbooks, however, the most common numerical approach is to solve the isofugacity equations together with the mass balances, often after considerable algebraic rearrangement. A flash calculation by minimization of the Gibbs function is interesting because it illustrates the direct application of a fundamental criterion in an actual computation.

The objective of this example is to solve an isothermal flash of a ternary mixture of n-hexane(1) + n-octane(2) + n-decane(3) using the Peng-Robinson equation of state by direct minimization of the Gibbs function. Figure 2(a) presents the information required to formulate the problem, i.e., the values of critical pressures and temperatures, acentric factors, binary interaction parameters (assumed equal to zero), temperature and pressure at equilibrium and the global number of moles of each substance in the system. The Gibbs function (G) of a system with two phases is:

$$G = \sum_{j=1}^2 \sum_{i=1}^c n_{ij} \mu_{ij} = \sum_{j=1}^2 \sum_{i=1}^c n_{ij} \left(\mu_i^{ig,pure}(T, P_0) + RT \ln \left(\frac{x_{ij} \hat{\phi}_{ij} P}{P_0} \right) \right) = \sum_{i=1}^c n_i \left(\mu_i^{ig,pure}(T, P_0) - RT \ln P_0 \right) + RT \sum_{j=1}^2 \sum_{i=1}^c n_{ij} \ln \left(x_{ij} \hat{\phi}_{ij} P \right) \quad (3)$$

where n_{ij} , x_{ij} , μ_{ij} , and $\hat{\phi}_{ij}$ represent the number of moles, mole fraction, chemical potential, and fugacity coefficient of component i in phase j . The symbols c , T , and P_0 denote the number of components, the temperature, and a reference pressure, respectively. The superscripts *ig* and *pure* refer to the ideal gas state and to a pure substance, respectively. From Eq. (3), it follows that:

$$\frac{\Delta G}{RT} = \frac{1}{RT} \left(\sum_{j=1}^2 \sum_{i=1}^c n_{ij} \mu_{ij} - \sum_{i=1}^c n_i \left(\mu_i^{ig,pure}(T, P_0) - RT \ln P_0 \right) \right) = \sum_{j=1}^2 \sum_{i=1}^c n_{ij} \ln \left(x_{ij} \hat{\phi}_{ij} P \right) \quad (4)$$

It can be shown that the minimum of $\frac{\Delta G}{RT}$ given by Eq. (4) corresponds to the phase equilibrium condition. Figure 2(b) shows the implementation of Eq. (4) with all the required intermediate steps. The numbers of moles of each component in the vapor phase (cells B16, C16, and D16) are taken as independent variables in the minimization problem, and the values in these cells in Fig. 2(b) are just initial guesses. The numbers of moles in the liquid phase (cells B15, C15, and D15) are calculated from the mass balances, i.e., by difference with respect to the specified total

amounts (cells B14, C14, and D14). The mole fraction cells, from B19 to D21, are computed using the values present in the mole number cells. Two array functions, *prlnphil* and *prlnphiv*, use the Peng-Robinson equation of state to compute the logarithms of the fugacity coefficients in the liquid and in the vapor phases, respectively. Please refer to Section 3.1 for details on the use of array functions in Excel[®]. The arguments in these functions are the universal gas constant, temperature, pressure, phase mole fractions (either liquid or vapor), and equation of state parameters (cells B2 to D7). The additional cells in the spreadsheet (B28 to D29, B32, and B33) represent the contribution of the liquid and vapor phases in the evaluation of Eq. (4). Cell B34 contains the cell to be minimized. Excel Solver is used to minimize cell B34 by modifying the values of cells B16, C16, and D16, as shown in Fig. 2(b). Figure 2(c) shows the spreadsheet after problem solution. By comparing Figs. 2(b) and 2(c), observe that the changes made by Excel Solver in the vapor mole numbers (cells B16, C16, and D16) propagate to the number of moles in the liquid phase, mole fractions, and all other physical properties. An interesting point to discuss in the classroom is that cells B28 and B29, C28 and C29, and D28 and D29 are pairwise equal because they are the natural logarithms of fugacities, i.e., students can observe the isofugacity criterion for phase equilibrium appearing naturally from a numerical, as opposed to analytical, formulation.

4. Use in Courses

A preliminary version of the program, with different installation procedure but similar functionality, was used during the spring of 2007 in the graduate course of Fluid Phase Equilibria (4 students) and in two sections of the undergraduate course of Chemical Engineering Thermodynamics (about 25 students) of the UAEU. The current version was used in the only

section of the undergraduate course of Chemical Engineering Thermodynamics (18 students) taught in the fall of 2007.

Because experience with XSEOS in graduate courses is limited, the discussion focuses on the undergraduate course of Chemical Engineering Thermodynamics at the UAEU. The first half of this course consists of a review of the first and second laws of thermodynamics followed by a discussion about free energies, residual and excess properties, and fugacity calculations. The second half the course focuses on formulating and solving phase equilibrium and chemical equilibrium problems. Students who take this course are usually familiar with using Excel[®] to program formulas and prepare plots.

Use of the program consisted of two types of activities related to phase equilibrium and, to a lesser extent, chemical equilibrium calculations: (a) instructor-guided classroom solution of problems with each student working in his/her own laptop computer and (b) development of a course project in groups of two or three students. These activities roughly took place during the final third of the course. Table 2 presents some of the projects students developed using XSEOS. Intrinsic numerical procedures available in Excel[®], such as *Goal Seek* and *Solver*, were used in these projects, but instructors and students willing to develop Newton-Raphson-based calculation procedures will find the analytical derivatives required by many problems already implemented in the package (Table 1).

Student feedback about the preliminary version of XSEOS was informal. A formal anonymous survey about the current version was answered by 16 out of the 18 students who took the undergraduate Chemical Engineering Thermodynamics course in the fall of 2007. Students should “strongly disagree” (1 point), “disagree” (2 points), “be neutral” (3 points), “agree” (4 points) or “strongly agree” (5 points) with each of seven statements presented to them.

Table 3 shows the statements and the corresponding average points. The first two statements intended to estimate the level of understanding acquired by using the program. They originated scattered opinions. Because the survey was anonymous, it was not possible to pinpoint the reason but a possible explanation is that students who led their project groups developed a deeper understanding of the methods and calculations. Statement 3 tried to gauge the reading and use of the program manual. Interestingly, students giving high grades in this statement tended to give high grades in the first two statements.

Statements 4 and 5 had to do with ease of installation in Excel[®] 2003 and 2007, respectively. In the spring of 2007, all students used Excel[®] 2003 but, in the fall, some students had already migrated to Excel[®] 2007 and they had installation problems. Statement 6 intended to measure the effectiveness of the sample calculations provided in the package. Statement 7 intended to assess the level of confidence for solving new problems and the results suggest that students are skeptical of their ability to do so.

In summary, for all statements, average points ranked between “neutral” and “agree”. Based on this feedback, the author has prepared movies (available in the Internet) that illustrate how to perform several types of calculations in XSEOS. This gives students the opportunity to review the calculation steps when needed. Furthermore, in future versions of the chemical engineering thermodynamics course, XSEOS will be used not only for phase and chemical equilibrium calculations but also during the first half of the course. The residual and excess functions available in the package allow the solution of many problems related to the first and second laws, such as the design of heat exchangers, turbines, compressors, expansion valves, among many others. This will give students more time and opportunities to use and understand the thermodynamic models available in the program.

5. Program Distribution

XSEOS is an Excel[®] add-in with approximately 20000 lines of VBA code at the time of its first public release. The Excel[®] add-in, a sample spreadsheet, a manual with installation procedures, and instructional videos are available at:

<http://www.engg.uaeu.ac.ae/mcastier/downloads.htm>

After installation, all functions of the thermodynamic package become available. A spreadsheet that uses these functions in applications such as bubble points, flash calculations, chemical equilibrium, energy balances, and speed of sound is also provided. XSEOS has open source code and is distributed under the GNU General Public License, version 3. Therefore, it is an expandable platform and will hopefully contribute to the exchange of experiences in the teaching of chemical engineering thermodynamics. XSEOS runs in Excel[®], which is part of the Microsoft[®] Office suite, available from Microsoft[®] resellers.

6. Areas for Collaboration

Areas for collaboration can be broadly organized around three issues: expandability, usability, and portability.

Expandability

Given the large number of thermodynamic models available and their wide range of applications, the set of models currently available in XSEOS reflects an arbitrary choice based on the wide use of some models and on the personal experience of the author with some others.

Many extensions can be envisaged. The most direct is to include additional models, but there are classes of models more immediately necessary. Among these are models for electrolyte

solutions, either excess Gibbs free energy (G^E) models or equations of state (EOS), and quantum mechanics based models, such as COSMO or one of its variations, as they may eventually replace conventional group contribution models for predictive phase equilibrium calculations. The creation of interfaces between XSEOS and external parameter databases for the models already available in XSEOS would be a useful extension to the package.

Usability

Examples that illustrate calculations such as the boiling point of pure substances, bubble points of mixtures, chemical equilibrium, speed of sound, and residual and excess properties are provided in the worksheets of the XSEOS spreadsheet files. User feedback may expand the set of examples available and contribute to improvements in interface and documentation.

Portability

The use of Excel[®] as development platform was primarily dictated by convenience, because it is widely available as part of the Microsoft[®] Office suite. The possibility of running XSEOS in freely available spreadsheets, such as Calc (part of Openoffice.org), will require porting the VBA code to other Basic dialects. Free online spreadsheet services, such as Google's spreadsheet, are currently unable to run XSEOS, but these services are evolving rapidly and, in the future, may have the features required by the package.

7. Final Comments and Perspectives

An Excel[®] add-in, XSEOS, that implements several excess Gibbs free energy models and equations of state has been developed, primarily for undergraduate education, but may also be useful for graduate education and research. Several traditional and modern thermodynamic models are available in the package. Students of the United Arab Emirates University who used

the package could quickly put together the solution of interesting course projects. XSEOS has open code and is freely available. This form of distribution will hopefully encourage other groups to contribute to the project. The package should be useful for instructors and students of chemical engineering thermodynamics courses.

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References

- [1] Smith, J.M., H.C. van Ness, and M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, 7th edition, McGraw-Hill, New York, 2005.
- [2] Sandler, S.I., Chemical, Biochemical, and Engineering Thermodynamics, 4th edition, Wiley, 2006.
- [3] Elliott, J.R. and C.T. Lira, Introductory Chemical Engineering Thermodynamics, Prentice-Hall PTR, 1999.
- [4] Koretsky, M.D., Engineering and Chemical Thermodynamics, Wiley, 2003.
- [5] Kyle, B.G., Chemical and Process Thermodynamics, 3rd edition, Prentice Hall PTR, 1999.

- [6] Cutlip, M.B. and M. Shacham, Problem Solving in Chemical and Biochemical Engineering with POLYMATH,TM Excel, and MATLAB®, 2nd edition, Prentice Hall, 2007.
- [7] Connelly, B., ThermoSolver: An Integrated Educational Thermodynamics Software Program, H.B.S. thesis, Oregon State University, 2006.
- [8] Vaidya S., <http://sourceforge.net/projects/vle-java/>, consulted on January 14th, 2008.
- [9] Ferreira, E.C., R. Lima, R. Salcedo, Spreadsheets in Chemical Engineering Education – a Tool in Process Design and Process Integration, *Int. J. Engng Ed.*, 20, 928-938, 2004.
- [10] Castier, M., Automatic implementation of thermodynamic models using computer algebra, *Computers and Chemical Engineering*, 23, 1229-1245, 1999.
- [11] Topliss, R.J., D. Dimitrelis, and J.M. Prausnitz, Computational Aspects of Non Cubic Equations of State for Phase Equilibrium Calculations Effects of Density Dependence Mixing Rules, *Computers and Chemical Engineering*, 12, 483-489, 1988.

Tables

Table 1. Thermodynamic models and properties currently available in XSEOS.

	G^E models	Equations of state
Models	Margules 2-, 3-, and 4- suffix* Regular solution theory Flory-Huggins Wilson TK-Wilson NRTL UNIQUAC UNIFAC Modified UNIFAC	van der Waals Redlich-Kwong Soave-Redlich-Kwong (SRK) Peng-Robinson Stryjek-Vera Predictive SRK (PSRK) Mattedi-Tavares-Castier
Properties	$\frac{g^E}{RT}, \frac{h^E}{RT}, \frac{s^E}{R}, \frac{c_p^E}{R},$ $\ln \gamma_i, \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_x, n \left(\frac{\partial \ln \gamma_i}{\partial n_j} \right)_{T, n_{k \neq j}}$	$P, \left(\frac{\partial P}{\partial \rho} \right)_{T, x}, \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{T, x}, \left(\frac{\partial^3 P}{\partial \rho^3} \right)_{T, x}, \ln \phi,$ $\ln \phi_i, \left(\frac{\partial \ln \phi_i}{\partial P} \right)_{T, x}, n \left(\frac{\partial \ln \phi_i}{\partial n_j} \right)_{T, P, n_{k \neq j}},$ $n \left(\frac{\partial V}{\partial n_j} \right)_{T, P, n_{k \neq j}}, \left(\frac{\partial \ln \phi_i}{\partial T} \right)_{P, x}, \left(\frac{\partial v}{\partial T} \right)_{P, x},$ $\frac{h^R}{RT}, \frac{s^R}{R}, \frac{c_p^R}{R}, \left(\frac{\partial P}{\partial T} \right)_{v, x}$

* The implemented Margules models work for binary mixtures only. All other models currently available in XSEOS work with any number of components.

Table 2. Examples of assignments and course projects solved using XSEOS.

Assignment/project	Thermodynamic properties	Models
Calculation of octanol + water partition coefficients	Activity coefficients at infinite dilution	UNIFAC
Vapor-liquid equilibrium of amine + water mixtures for carbon dioxide absorption	Activity coefficients	UNIQUAC, NRTL
Properties of refrigerants that may replace CFCs (chlorofluorocarbons)	Fugacity coefficients, residual enthalpies	Cubic EOS
Compositional segregation of mixtures under gravitational and centrifugal fields	Fugacity coefficients	Cubic EOS
Vapor liquid equilibrium of chlorine + hydrogen chloride and nitrosyl chloride + ethyl acetate mixtures	Fugacity coefficients	PSRK EOS
Chemical equilibrium in multireaction system	Fugacity coefficients	PSRK EOS

Table 3. Opinion survey with the undergraduate students of Chemical Engineering
Thermodynamics, Fall 2007, United Arab Emirates University.

*Point scale: “strongly disagree” (1 point), “disagree” (2 points),
“neutral” (3 points), “agree” (4 points) or “strongly agree” (5 points)*

Statement	Average points
1. The XSEOS package helped me understand how to perform physical property and equilibrium calculations.	3.4
2. I understood the calculations I made using the XSEOS package.	3.7
3. I read or consulted the User's Manual provided with the XSEOS package.	3.4
4. Installation in Excel [®] 2003 was easy and unproblematic (answer this question only if you used Excel [®] 2003).	3.7
5. Installation in Excel [®] 2007 was easy and unproblematic (answer this question only if you used Excel [®] 2007).	3.1
6. The examples in the Excel [®] spreadsheet are easy to follow.	3.5
7. I would know how to organize the solution of a new problem in XSEOS, similar but not identical to a problem of the sample spreadsheet.	3.2

Figure captions

Fig. 1. Bubble point calculations using the UNIQUAC model.

	A	B	C	D	E	F	G	H	I	J
1	methanol(1)+water(2)									
2		R	T(K)							
3		8.314	333.15							
4	r	1.4311	0.92							
5	q	1.432	1.4							
6	a(l,j) (J/mol)	0	-1777		P1sat (kPa)	84.562				
7		2981	0		P2sat (kPa)	19.953				
8										
9		x1	x2	lngama1	lngama2	gama1	gama2	P (kPa)	y1	y2
10		0	1							

Fig.1(a). Spreadsheet before the beginning of calculations.

	A	B	C	D	E	F	G	H	I	J
1	methanol(1)+water(2)									
2		R	T(K)							
3		8.314	333.15							
4	r	1.4311	0.92							
5	q	1.432	1.4							
6	a(l,j) (J/mol)	0	-1777		P1sat (kPa)	84.562				
7		2981	0		P2sat (kPa)	19.953				
8										
9		x1	x2	lngama1	lngama2	gama1	gama2	P (kPa)	y1	y2
10		0	1	=uniquac(

Fig.1(b). The user *must mark* the cells for $\ln \gamma_1$ and $\ln \gamma_2$ *before* typing the call of function uniquac.

	A	B	C	D	E	F	G	H	I	J
1	methanol(1)+water(2)									
2		R	T(K)							
3		8.314	333.15							
4	r	1.4311	0.92							
5	q	1.432	1.4							
6	a(l,j) (J/mol)	0	-1777		P1sat (kPa)	84.562				
7		2981	0		P2sat (kPa)	19.953				
8										
9		x1	x2	lngama1	lngama2	gama1	gama2	P (kPa)	y1	y2
10		=uniquac(\$B\$3,\$C\$3,B10:C10,\$B\$4:\$C\$7)								

Fig.1(c). UNIQUAC function call.

	A	B	C	D	E	F	G	H	I	J
1	methanol(1)+water(2)									
2		R	T(K)							
3		8.314	333.15							
4	r	1.4311	0.92							
5	q	1.432	1.4							
6	a(l,j) (J/mol)	0	-1777		P1sat (kPa)	84.562				
7		2981	0		P2sat (kPa)	19.953				
8										
9		x1	x2	lngama1	lngama2	gama1	gama2	P (kPa)	y1	y2
10		0	1	0.867	0.000					

Fig.1(d). Numerical values after the UNIQUAC function call.

	A	B	C	D	E	F	G	H	I	J
1	methanol(1)+water(2)									
2		R	T(K)							
3		8.314	333.15							
4	r	1.4311	0.92							
5	q	1.432	1.4							
6	a(l,j) (J/mol)	0	-1777		P1sat (kPa)	84.562				
7		2981	0		P2sat (kPa)	19.953				
8										
9		x1	x2	lngama1	lngama2	gama1	gama2	P (kPa)	y1	y2
10		0	1	0.867	0.000	2.380	1.000	19.953	0	1

Fig.1(e). Set of results for the specified liquid phase composition.

	A	B	C	D	E	F	G	H	I	J
1	methanol(1)+water(2)									
2		R	T(K)							
3		8.314	333.15							
4	r	1.4311	0.92							
5	q	1.432	1.4							
6	a(l,j) (J/mol)	0	-1777		P1sat (kPa)	84.562				
7		2981	0		P2sat (kPa)	19.953				
8										
9		x1	x2	lngama1	lngama2	gama1	gama2	P (kPa)	y1	y2
10		0	1	0.867	0.000	2.380	1.000	19.953	0	1
11		0.25	0.75	0.324	0.067	1.383	1.089	45.232179	0.6461642	0.3538358
12		0.5	0.5	0.109	0.191	1.115	1.210	59.215951	0.7960597	0.2039403
13		0.75	0.25	0.022	0.331	1.022	1.393	71.776916	0.9031892	0.0968108
14		1	0	0.000	0.478	1.000	1.612	84.562	1	0

Fig.1(f). Complete set of results.

Fig. 2. Flash calculation of a ternary mixture using the Peng-Robinson equation of state.

	A	B	C	D	E
1		<i>n-C6(1)</i>	<i>n-C8(2)</i>	<i>n-C10(3)</i>	
2	<i>Tc(K)</i>	507.5	568.8	617.7	
3	<i>Pc(bar)</i>	30.1	24.9	21.2	
4	<i>omega</i>	0.299	0.398	0.489	
5	<i>kij</i>	0.0	0.0	0.0	
6		0.0	0.0	0.0	
7		0.0	0.0	0.0	
8					
9	<i>R (bar.cm3/(mol.K))</i>	83.14			
10	<i>Temperature (K)</i>	450			
11	<i>Pressure (bar)</i>	4.5			
12					
13	<i>Moles</i>	<i>n-C6(1)</i>	<i>n-C8(2)</i>	<i>n-C10(3)</i>	<i>Total</i>
14	<i>Global</i>	40	30	30	100.000

Fig.2(a). Spreadsheet before the beginning of calculations.

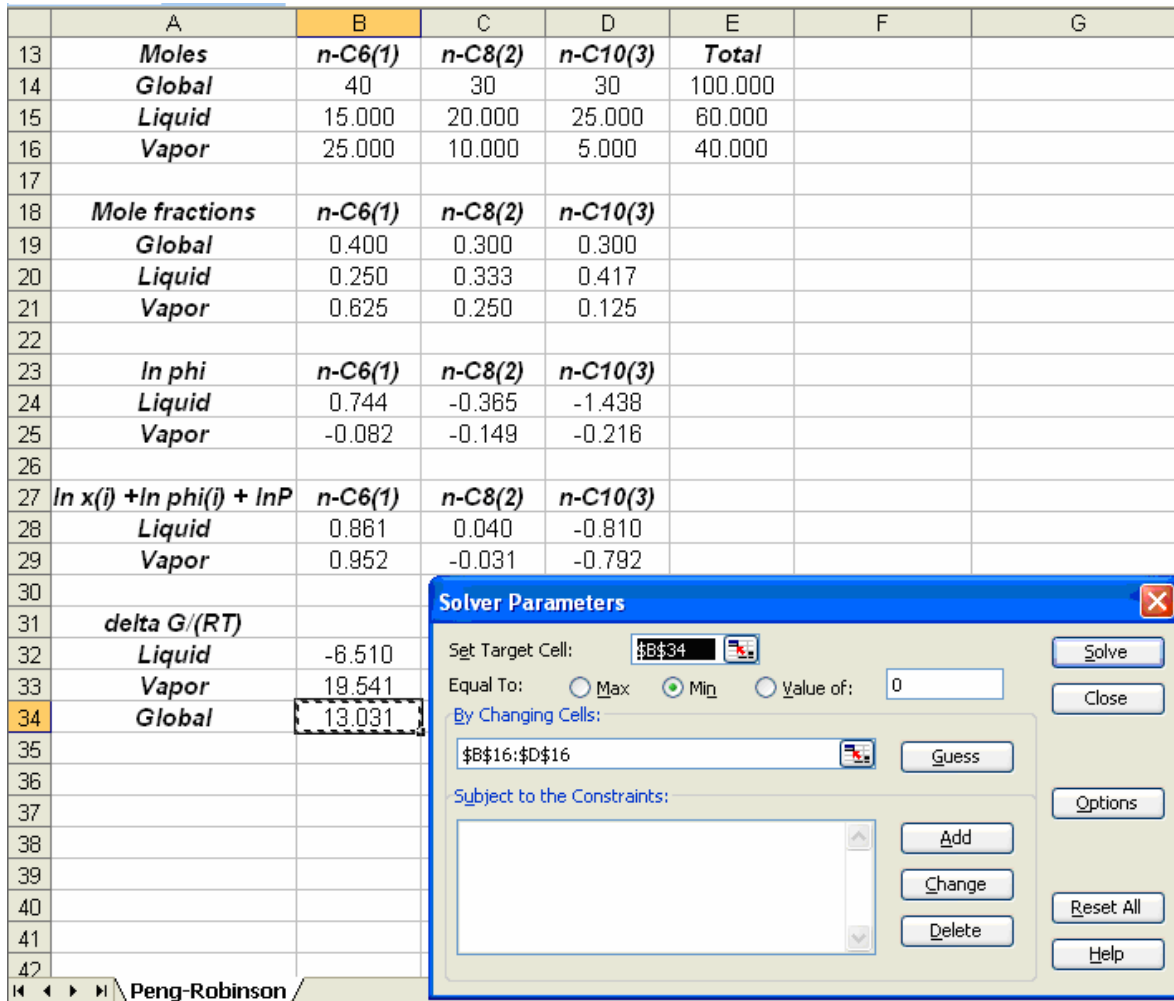


Fig.2(b). Spreadsheet with initial guess before the minimization.

	A	B	C	D	E
13	Moles	n-C6(1)	n-C8(2)	n-C10(3)	Total
14	Global	40	30	30	100.000
15	Liquid	17.206	20.436	25.613	63.255
16	Vapor	22.794	9.564	4.387	36.745
17					
18	Mole fractions	n-C6(1)	n-C8(2)	n-C10(3)	
19	Global	0.400	0.300	0.300	
20	Liquid	0.272	0.323	0.405	
21	Vapor	0.620	0.260	0.119	
22					
23	In phi	n-C6(1)	n-C8(2)	n-C10(3)	
24	Liquid	0.743	-0.365	-1.438	
25	Vapor	-0.082	-0.149	-0.216	
26					
27	ln x(i) + ln phi(i) + ln P	n-C6(1)	n-C8(2)	n-C10(3)	
28	Liquid	0.945	0.009	-0.838	
29	Vapor	0.945	0.009	-0.838	
30					
31	delta G/(RT)				
32	Liquid	-5.009			
33	Vapor	17.952			
34	Global	12.943			

Fig.2(c). Spreadsheet with the problem solution.

Biographical sketch

Marcelo Castier obtained his B.Sc. (1981) and M.Sc. (1985) degrees in chemical engineering at the Federal University of Rio de Janeiro (UFRJ), Brazil, and his Ph.D. (1988) at the Technical University of Denmark. He joined UFRJ as a faculty member in 1988, from where he moved to the United Arab Emirates University, in 2006. Marcelo has supervised or co-supervised 20 M.Sc. dissertations and 5 D.Sc. theses and authored more than 60 papers in peer-reviewed journals. His teaching and research focus in the areas of chemical engineering thermodynamics and process design.