

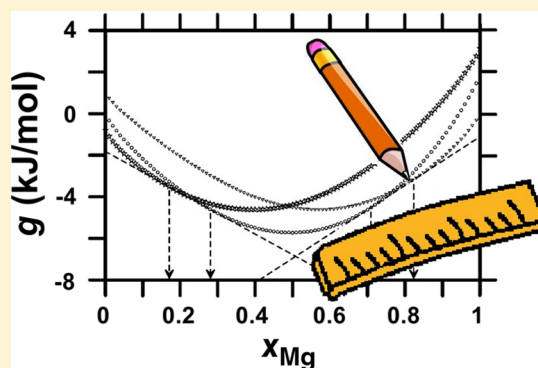
# Deconstructing Phase Diagram Calculations

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## S Supporting Information

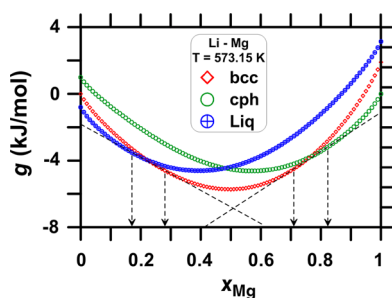
**ABSTRACT:** Phase diagram calculations are an important topic in material science. They are usually carried out with limited-distribution software packages. This technology report is an introduction to software based phase diagram calculations. Three spreadsheets calculators are presented. The first one plots the Gibbs free energy versus composition for Al–Zn, Li–Mg, and Pelton’s fictional A–B alloy. The second one calculates equilibrium phase composition for A–B. The third one calculates the Li–Mg temperature–composition diagram. The coding is reduced to a minimum and calculations are directly accessible to the user. The programs aim to be practice tools to complement instructor’s lectures.



**KEYWORDS:** Graduate Education/Research, Upper-Division Undergraduate, Physical Chemistry, Calculator-Based Learning, Thermodynamics, Phases/Phase Transitions/Diagrams

Phase diagrams are an important graphical method in material science. Numerous resources introducing phase diagram calculations (PDC), including historical developments, are available.<sup>1–9</sup>

The criterion for phase stability is conceptually simple.<sup>10</sup> Stable phases are easily spotted on a Gibbs free energy–composition plot, using the common tangency rule (Figure 1).



**Figure 1.** Gibbs free energy plot for Li–Mg binary alloy at  $T = 573.15$  K. The common tangency rule helps to identify the two-phase equilibria: Liq = bcc with  $x_{\text{Mg}}(\text{Liq}) = 0.1706$  and  $x_{\text{Mg}}(\text{bcc}) = 0.2806$ ; bcc = cph with  $x_{\text{Mg}}(\text{bcc}) = 0.7099$  and  $x_{\text{Mg}}(\text{cph}) = 0.8232$ , where bcc stands for Body-centered cubic and cph for compact hexagonal.

But PDC are still a complex task that requires limited-distribution software packages. Users must become familiar with a more-or-less challenging interface and with calculation algorithms not readily accessible. To the best knowledge of the author, educational material bridging the gap between introductory level concepts, as illustrated by Figure 1, and use of advanced level, that is, professional- or research-grade software packages, is scarce. As noted by Demoin et al.,

instructors benefit from open-distribution, ready-made resources to support concept learning.<sup>11</sup>

This technology report is an introduction to PDC using Microsoft Excel spreadsheets. The spreadsheet format enables a clear and concise layout of procedures and relatively accurate calculations are carried out with minimal coding.

The main concepts required for a complete understanding of PDC are embedded in iconic Figure 1, namely, (i) the Gibbs free energy model and (ii) common tangency numerical analysis. The next section focuses on the thermodynamics concepts, with the section following addressing the numerical analysis problem.

## THERMODYNAMICS CONCEPTS: GIBBS FREE ENERGY

The first requirement is the availability of a Gibbs free energy model. It is determined by calculations or experiments. PDC are often carried out by research laboratories, and the models are communicated in scientific publications.<sup>12,13</sup> As an illustration, consider the calculation of the Li–Mg phase diagram. A literature search resulted in the model<sup>12</sup> investigated by Saunders<sup>12</sup> (see Appendix 1 in the Supporting Information).

The molar Gibbs energy for a binary alloy A–B is usually modelled with eq 1.

$$g(x_A, T) = x_A g_A^{\text{ref}} + (1 - x_A) g_B^{\text{ref}} + g_{\text{mix}}^{\text{xs}} - RT \{ x_A \log_e x_A + (1 - x_A) \log_e (1 - x_A) \} \quad (1)$$

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where  $x_A$  is element A mole fraction,  $T$  is the temperature in Kelvin,  $R$  is the gas constant,  $g_A^{\text{ref}}$  and  $g_B^{\text{ref}}$  are the molar Gibbs free energy of the pure elements A and B, respectively, and  $g_{\text{mix}}^{\text{xs}}$  is the excess term.<sup>14</sup> The first two terms of eq 1 correspond to noninteracting pure elements. The last term of eq 1 is an ideal entropic contribution derived from statistical thermodynamics. Finally,  $g_{\text{mix}}^{\text{xs}}$  is an adjustment parameter that is described by a large variety of equations.<sup>1,2</sup> The criterion of choice during a model investigation is to select the one that fits  $g(x_A, T)$  best.

For Li–Mg, Saunders publication indicates that the excess term is best described by a Redlich–Kister polynomial series. To be more specific, the Li–Mg liquid-phase  $g_{\text{mix}}^{\text{xs}}$  is described by

$$g_{\text{mix}}^{\text{xs}} = x_A(1 - x_A)(L_0 + L_1(2x_A - 1) + L_2(2x_A - 1)^2) \quad (2a)$$

$$L_0 = -14935 + 10.371T \quad (2b)$$

$$L_1 = -1789 + 1.143T \quad (2c)$$

$$L_2 = 6533 - 6.6915T \quad (2d)$$

where  $g_{\text{mix}}^{\text{xs}}$  is in J/mol and  $T$  in Kelvin. Gibbs free energy of the Li–Mg liquid phase is then calculated by combining eqs 1 and 2a–2d. Similar steps apply for the Li–Mg solid phases. The resulting Gibbs curves are shown in Figure 1 for  $T = 573.15$  K.

The model is a little cumbersome in size but it is not complex from a mathematical perspective. Spreadsheets handle eqs 1 and 2a–2d without difficulty and plots are set up in a reasonable amount of time.

The Li–Mg, Al–Zn, and Pelton's A–B PDC spreadsheets, available in the Supporting Information, are good practice vehicles for the tangency rule. The dynamic link between  $g(x_A, T)$  and  $T$  clearly advantages the spreadsheet approach over textbook static diagrams as teaching device. Sketching of a phase diagram is also possible by collecting phase compositions at several temperatures. This approach makes the common tangent method more real, while stressing the need for a calculator to get fast, accurate values. Practice on varied examples further enforces the learning of the common tangency concept.

The fictional A–B binary alloy is approximated with a regular solution. The parameters are those used by Pelton to introduce topological changes in phase diagrams. A student can compare sketched (Gibbs free energy–composition) plots to Pelton's diagrams or an instructor can use it as a vehicle for varied case studies.<sup>15</sup>

## NUMERICAL ANALYSIS

Application of the common tangency rule with a ruler and a pencil is deceptively simple compared to the resolution of the mathematical problem. The algebraic method of Iglesias-Silvia et al. is applied to solve the problem.<sup>16</sup> Coupled  $F_1$  and  $F_2$  functions are minimized to calculate phase compositions

$$F_1 = \frac{\partial g_\alpha}{\partial x_A} - \frac{\partial g_\beta}{\partial x'_A} \quad (3a)$$

$$F_2 = (g_\beta - g_\alpha) - (x'_A - x_A) \left( \frac{\partial g_\alpha}{\partial x_A} \right) \quad (3b)$$

where  $x_A$  is the mole fraction of element A in phase  $\alpha$  of molar Gibbs free energy  $g_\alpha$  and  $x'_A$  is the mole fraction of element A in

phase  $\beta$  of molar Gibbs free energy  $g_\beta$ . When phase  $\alpha$  and  $\beta$  are in equilibrium,  $F_1 = 0$  and  $F_2 = 0$ . The calculation of  $\partial g/\partial x$  for any phase is trivial because the  $g(x_A, T)$  model is known.

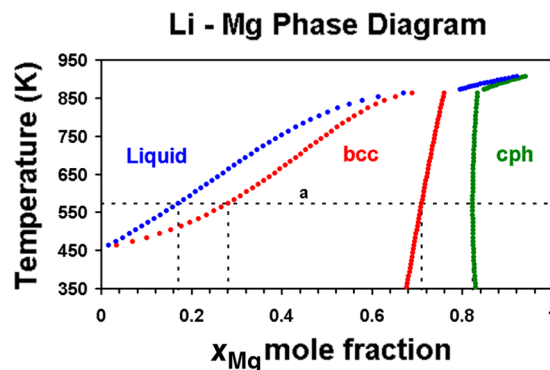
The  $F_1 = 0$  criterion is a direct translation of the common tangent rule. But  $F_1 = 0$  is not enough to unequivocally calculate equilibrium compositions. The additional criterion  $F_2 = 0$  offers a safeguard against parallel tangents.  $F_2$  is the cancellation of the tangent value, by the slope of the line connecting the couple phases.

Equilibrium compositions are obtained with a multidimensional Newton–Raphson procedure described by

$$\begin{pmatrix} x_{A,n+1} \\ x'_{A,n+1} \end{pmatrix} = \begin{pmatrix} x_{A,n} \\ x'_{A,n} \end{pmatrix} - \begin{pmatrix} \frac{\partial^2 g_\alpha}{\partial x_A^2} & -\frac{\partial^2 g_\beta}{\partial x_A'^2} \\ (x_A - x'_A) \frac{\partial^2 g_\alpha}{\partial x_A^2} & \frac{\partial g_\beta}{\partial x'_A} - \frac{\partial g_\alpha}{\partial x_A} \end{pmatrix}^{-1} \begin{pmatrix} F_1 \\ F_2 \end{pmatrix} \quad (4)$$

where  $\alpha$  stands for phase 1 and  $\beta$  for phase 2,  $x_A$  is the mole fraction of element A in phase 1, and  $x'_A$  is the mole fraction of element A in phase 2. Calculation of first and second partial derivatives is straightforward for the  $g(x_A, T)$  model dealt with in this report. Spreadsheets have the capability of also handling matrix operations, and the calculations can be arranged in a reasonable amount of time.

For sake of simplicity, a coarse automated numerical analysis is used in the programs in the Supporting Information. Figure 2



**Figure 2.** Li–Mg phase diagram calculated with the spreadsheet. The dashed lines are a guide for equilibrium values at 573.15 K shown in Figure 1

shows the Li–Mg phase diagram calculated with the spreadsheet. A simple Visual Basic Application macro is used, and little programming experience is required to understand the code. For each iteration, the macro transfers the output values to the input cells. The algorithm is not sophisticated, and any skilled user will find it easy to transfer the algorithm to another platform or to adapt it to other material systems.

The simplified calculators, with user's contribution, cover two major tasks performed by advanced software packages, namely, thermodynamic analysis and numerical analysis. Practice with those gives a better understanding of the calculation methods, without recurring to specialty software. They are also the opportunity to stress what matters for a phase diagram calculation from a chemical perspective: the derivation of the free energy model.

## ■ ASSOCIATED CONTENT

### 📎 Supporting Information

Spreadsheets for calculating phase diagrams. This material is available via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Saunders, N.; Miodownik, P. *Calphad (Calculation of Phase Diagrams): A Comprehensive Guide*, Pergamon Materials Series; Cahn, R. W., Ed.; Pergamon, Elsevier Science Ltd: Oxford, 1998; Vol. 1.
- (2) Lukas, H. L.; Fries, S. G.; Sundman, B. *Computational Thermodynamics, The Calphad Method*; Cambridge University Press: Cambridge, 2007.
- (3) Lukas, H. L.; Weiss, J.; Henig, E.-Th. Strategies for the Calculation of Phase Diagrams. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **1982**, *6*, 229–251.
- (4) Lin, L.; Wollants, P.; Van Der Biest, O.; Delaey, L. A Simple Method for the Calculation of Equilibrium Phase Diagrams. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **1994**, *18*, 89–98.
- (5) Peckham, G. D.; McNaught, I. J. An Introductory Idea for Teaching Two-Component Phase Diagrams. *J. Chem. Educ.* **2011**, *88*, 592–593.
- (6) Berndt, A. Binary Phase Diagrams. *J. Chem. Educ.* **1969**, *46*, 594.
- (7) Jones, G. L. A Unified Quantitative Interpretation of Two-Component Phase Diagrams. *J. Chem. Educ.* **1963**, *40*, 38.
- (8) Clerc, D. G.; Cleary, D. A. Spinodal Decomposition as an Interesting Example of the Application of Several Thermodynamic Principles. *J. Chem. Educ.* **1995**, *72*, 112–115.
- (9) Sanders, P. C.; Reeves, J. H.; Messina, M. The Binary Temperature–Composition Phase Diagram. *J. Chem. Educ.* **2006**, *83*, 150–154.
- (10) Mackowiak, J. *Physical Chemistry for Metallurgists*; American Elsevier Publishing Company, Inc.: New York, 1966; reprinted with corrections.
- (11) Demoin, D. W.; Jurisson, S. S. Chemical Kinetics Laboratory Discussion Worksheet. *J. Chem. Educ.* **2013**, *90*, 1200–1202.
- (12) Saunders, N. A Review and Thermodynamic Assessment of The Al–Mg and Mg–Li systems. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **1990**, *14*, 61–70.
- (13) Chen, S. L.; Chang, Y. A. A Thermodynamic Analysis of the Al–Zn System and Phase Diagram Calculation. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **1993**, *17*, 113–124.
- (14) Equation 1 is very similar to eq 3.66 of reference 1 (page 53), eq 5.1 of reference 2 (page 80), and equation 1 of reference 12.
- (15) Pelton, A.D. *Phase Diagrams in Physical Metallurgy*, 3rd ed.; Cahn, R.W., Haasen, P., Eds.; North Holland: New York, 1983; pp 328–81, figure 8 page 338.
- (16) Iglesias-Silva, G. A.; Bonilla-Petriciolet, A.; Eubank, P. T.; Holste, J. C.; Hall, K. R. An Algebraic Method that Includes Gibbs Minimization for Performing Phase Equilibrium Calculations for Any Number of Components or Phases. *Fluid Phase Equilib.* **2003**, *210*, 229–245.