

# SPREADSHEETS FOR THERMODYNAMICS INSTRUCTION

## *Another Point of View*

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In the article "Spreadsheets for Thermodynamics Instruction," Savage<sup>[1]</sup> makes an excellent case for the use of computational tools in the undergraduate thermodynamics course. Indeed, computational tools are necessary if one is to do calculations with fluids other than the ideal gas or the incompressible fluid. It would be difficult to argue against using computational tools in thermodynamics instruction and more generally throughout the undergraduate curriculum.

A point of debate, however, is what type of computational tool should be used. In the above-mentioned article, Savage considers two types of computational tools: spreadsheets, such as LOTUS or EXCEL, and specially prepared programs, such as the BASIC programs in my textbook.<sup>[2]</sup> The point of this short note is to suggest a third alternative and to open what I hope will be a discussion in *CEE* of the best computational tools for use in an undergraduate instruction fundamentals course.

Having students write their own computer programs to solve many different types of problems, which requires not only an understanding of the course fundamentals but also of numerical analysis and computer programming, is too much to demand in an undergraduate course. A problem with using instructor-prepared programs (such as the BASIC language programs in my textbook) is that the student is presented with a black-box computer code that he or she has not written and probably does not understand. I have found that while students greatly appreciate such programs, many have little interest in learning how the fundamentals of the course have been used to make a working computer program.

The use of instructor-prepared spreadsheets, as described by Savage, does not solve this problem. Further, it can be argued that in spite of their ability to solve some equations and consequently some thermodynamics problems, spreadsheets are not the natural tool for such calculations. While



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instructor-prepared spreadsheets may provide some flexibility, for example, in the choice of independent variables, they do not address the underlying problem of the student's failure to understand what is being done in the calculation.

Since finding the answer to most thermodynamics problems involves solving equations, an equation-solving program would seem to be a more natural tool to use than a spreadsheet. As evidence of this, I consider only one of the examples Savage used (which happens to be Illustration 4.7-1 from my textbook) and use only one equation-solving program, MATHCAD. There are many other commercially available equation-solving programs, such as MATHEMATICA, MAPLE, MATLAB, and others. But because of its ease of use and low cost, I have chosen to use MATHCAD for this discussion.

The problem statement, including all equations, is as follows:

Nitrogen gas is being withdrawn from a 0.15-m<sup>3</sup> cylinder at the rate of 10 mol/min. The cylinder initially contains the gas at a pressure of 100 bar and 170 K. The cylinder is well insulated and there is negligible heat transfer between the cylinder walls and the gas. How many moles of gas will be in the cylinder after 50 minutes, and what will be the temperature and pressure of the gas? The gas is assumed to be described by the Peng-Robinson<sup>[3]</sup> equation of state

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)}$$

**TABLE 1**  
**Illustration 4.7-1 with MATHCAD**

**Property Data**  
(T in K, P in bar):

$$T_c := 126.2 \quad P_c := 33.94 \quad \omega := 0.04 \quad C_{p1} := 27.2 \quad C_{p2} := 0.0042$$

$$R := 0.00008314 \quad k_a := 0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega \cdot \omega$$

**Initial Conditions** (vt=total volume, m<sup>3</sup>):

$$T_i := 170 \quad P_i := 100 \quad v_t := 0.15$$

**Peng Robinson Constants:**

$$b := 0.07780 \cdot \frac{R \cdot T_c}{P_c} \quad a_c := 0.45724 \cdot \frac{R^2 \cdot T_c^2}{P_c}$$

**Initial Temperature:**

$$T := T_i$$

Note that these are being defined as a function of temperature since we will need to iterate on temperature later to obtain the final state of the system.

$$\text{alf}(T) := 1 \cdot \left[ 1 + k_a \cdot \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad a(T) := a_c \cdot \text{alf}(T) \quad D_a(T) := \frac{d}{dT} a(T)$$

**Find initial molar volume and number of moles.**  
Start with initial guess for volume, m<sup>3</sup>/mol

$$V := \frac{R \cdot T_i}{P_i}$$

**Solve P-R EOS for initial volume:**

$$\text{Given} \quad P_i = \frac{R \cdot T}{V - b} - \frac{a(T)}{V \cdot (V + b) + b \cdot (V - b)} \quad V_i := \text{Find}(V)$$

**Initial molar volume and number of moles**

$$V_i = 9.567 \cdot 10^{-5} \quad N_i := \frac{v_t}{V_i} \quad N_i = 1.568 \cdot 10^3$$

**Entropy departure at the initial conditions**

$$\text{DELS}_i := \left[ R \cdot \ln \left[ (V_i - b) \cdot \frac{P_i}{R \cdot T} \right] + \frac{D_a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln \left[ \frac{V_i + (1 + \sqrt{2}) \cdot b}{V_i + (1 - \sqrt{2}) \cdot b} \right] \right] \cdot 10^5$$

**Now consider final state**

$$N_f := N_i - 10 \cdot 50 \quad V_f := \frac{v_t}{N_f} \quad V := V_f$$

**Type out final number of moles and specific volume**

$$N_f = 1.068 \cdot 10^3 \quad V_f = 1.405 \cdot 10^{-4}$$

**Final pressure, will change in course of solving for the final temperature**

$$P_f(T) := \frac{R \cdot T}{V - b} - \frac{a(T)}{V \cdot (V + b) + b \cdot (V - b)}$$

**Entropy departure at final conditions**

$$\text{DELS}(T) := \left[ R \cdot \ln \left[ (V - b) \cdot \frac{P_f(T)}{R \cdot T} \right] + \frac{D_a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln \left[ \frac{V + (1 + \sqrt{2}) \cdot b}{V + (1 - \sqrt{2}) \cdot b} \right] \right] \cdot 10^5$$

**Solve for final temperature using S(final)-S(initial)=0**

$$\text{Given} \quad 0 = 27.2 \cdot \ln \left( \frac{T}{T_i} \right) + 0.0042 \cdot (T - T_i) - R \cdot 10^5 \cdot \ln \left( \frac{P_f(T)}{P_i} \right) + \text{DELS}(T) - \text{DELS}_i$$

$$T := \text{FIND}(T)$$

**Type out solution**

$$T = 134.66 \quad P_f(T) = 40.561$$

where

$$b = 0.07780 \frac{RT_c}{P_c} \quad a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T)$$

$$\alpha(T) = \left( 1 + \kappa \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right)^2$$

In these equations,  $T_c$  and  $P_c$  are the critical temperature and pressures, respectively;  $R$  is the gas constant; and  $\kappa = 0.37464 + 1.54226 \omega - 0.26992 \omega^2$ , where  $\omega$  is the acentric factor. Also,  $P$  is pressure,  $T$  is temperature, and  $V$  is the molar volume. Finally, the ideal heat capacity of nitrogen is approximated by

$$C_p^*(J/mol K) = 27.2 + 4.2 \times 10^{-3} T (\text{in K})$$

The solution to this problem involves the following steps:

1. Given the initial temperature and pressure,  $T$  and  $P$ , solve the equation of state for the initial molar volume ( $V_i$ ). Knowing  $V_i$  and the volume of the tank ( $v_t$ ), calculate the initial number of moles of gas in the tank,  $N_i = v_t/V_i$ .
2. From the mass balance and the known gas molar removal rate, compute the number of moles of gas in the tank after fifty minutes ( $N_f = N_i - 50 \times 10$ ) and the final molar volume ( $V_f = v_t/N_f$ ).
3. Now having the final molar volume  $V_f$ , the value of one other state variable is needed to fix the final state of the system. This is obtained from the entropy balance that shows that the molar entropy the gas remaining in the tank is constant. This is  $S(T_f, P_f) = S(T_i, P_i)$  or  $0 = S(T_f, P_f) - S(T_i, P_i)$ . In terms of the equation of state, this relation is

$$\begin{aligned} 0 &= S(T_f, P_f) - S(T_i, P_i) \\ &= S^{IG}(T_f, P_f) + [S(T_f, P_f) - S^{IG}(T_f, P_f)] \\ &\quad - [S(T_i, P_i) - S^{IG}(T_i, P_i)] \\ &= S^{IG}(T_f, P_f) - S^{IG}(T_i, P_i) \\ &\quad + [S(T_f, P_f) - S^{IG}(T_f, P_f)] - [S(T_i, P_i) - S^{IG}(T_i, P_i)] \\ &= \int_{170 \text{ K}}^{T_f} \frac{C_p^*}{T} dT - R \int_{100 \text{ bar}}^{P_f} \frac{dP}{P} + [S(T_f, P_f) - S^{IG}(T_f, P_f)] \\ &\quad - [S(T_i, P_i) - S^{IG}(T_i, P_i)] \\ &= 27.2 \ln \left( \frac{T_f}{170} \right) + 0.0042 \times (T_f - 170) - R \ln \left( \frac{P_f}{100} \right) \\ &\quad + [S(T_f, P_f) - S^{IG}(T_f, P_f)] - [S(T_i, P_i) - S^{IG}(T_i, P_i)] \end{aligned}$$

For the Peng-Robinson equation of state, the entropy separ-

ture term is

$$\begin{aligned} \text{DelS} &= S(T, P) - S^{IG}(T, P) \\ &= R \ln \left[ (V - b) \frac{P}{RT} \right] + \frac{da(T)}{2\sqrt{2}b} \ln \left[ \frac{V + (1 + \sqrt{2})}{V + (1 - \sqrt{2})} \right] \end{aligned}$$

Here, the final specific volume is known and the final temperature and pressure are unknown. These two variables must satisfy the volumetric equation of state and the entropy balance above. This problem is nonlinear in these variables, and it is for such problems that an equation-solving package is especially useful.

Table 1, which occupies a single page, contains the MATHCAD formulation of the problem, the documentation (in bold letters), and the solution. The reason for presenting here all the equations for the solution to this problem is to enable the reader to see how the equations to be solved and the MATHCAD syntax are almost identical.

Students can quickly develop their own worksheets and solve problems using an equation-solving package. To do this, they need to understand the problem they are trying to solve, should know very little of the MATHCAD syntax (instead of a complicated programming language), and know little or nothing about numerical analysis. The emphasis will then be on understanding the fundamentals of the problem to be solved rather than on the mechanics of solving the resulting equations. I believe this to be of important pedagogic advantage in using equation-solving packages for basic chemical engineering courses.

Savage mentions that the problem used for illustration here took about thirty seconds to solve using a spreadsheet on a Mac IIsi; the solution is obtained essentially instantaneously on a WINDOWS-based machine with a 486 75 MHz processor with MATHCAD PLUS 6.0. Further, I was able to develop the MATHCAD worksheet in Table 1 and to obtain a solution to the problem in a very short time, even though I am a novice at using this package.

An advantage of using computer-based methods in thermodynamics is that the tediousness of solving problems involving realistic equations of state is avoided. Another is that computational errors can be avoided. This is demonstrated by the fact that while answers from Savage's spreadsheet solution and the MATHCAD solution presented here are in complete agreement with each other, they do not agree with the manual iterative solution in my textbook, which, in fact, is in error for the reason mentioned by Savage.

## REFERENCES

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3. Peng, D.Y., and Robinson, *Ind. Eng. Chem. Fund.*, **15**, 59 (1976) □