

Editorial Note: The “Class and Home Problems” section on pages 366-368 of the Fall 2000 issue of CEE presented Erich A. Muller’s article, “A Thermodynamics Problem with Two Conflicting Solutions.” In it, tanks A (isothermal) and B (adiabatic) are filled with an ideal gas and connected by pipes and a valve. Initially, $p_A > p_B$. If the valve is opened and equilibrium attained, will it have been necessary to add (or remove) heat from tank A? Professor Muller’s article has elicited the following two letters. His reply is also appended.

We appreciate the interest that Professor Muller’s problem has generated, and request that any further correspondence on this problem be e-mailed to him at

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To the Editor:

The recent article by Müller^[1] presents an interesting discussion of pedagogically important issues. We wish to comment on two aspects of the article. First, we believe that it is pedagogically more sound to treat Müller’s “two conflicting solutions” as (non-conflicting) solutions to different problems that arise from two different equilibrium *models* of the situation, as implied in his comments. Second, we believe that his “Comments on the Equation for the Uniform State, Uniform Flow Model” can be improved regarding the basic assumptions underlying use of the unsteady-state energy-balance equation for a control volume and its general application in first-law analysis. We elaborate on both these points in the following.

Concerning the analysis of the situation described in the article, we note that his “Solution #1” relates to a model in which it is stated that “tank B is adiabatic”; that is, there is no heat transfer to or from tank B ($\dot{Q} = 0$) at any time to any other body, although this does not preclude exchange of energy via flow of matter through the connecting line and valve. Practically speaking, the equilibrium state for the contents of tank B is a partial equilibrium state with respect to the contents of tank A: mechanical, but not thermal, equilibrium. Regardless of where the control surface is placed (around tank A alone or around tanks A and B together), the conclusion reached is as Müller states: $Q^A > 0$. Solution #1 is the solution to the problem arising from one particular model of the situation.

His “Solution #2” relates to a different model of the situation, in which it is stated that there is “a heat transfer between the tanks” (presumably through the connecting line and valve). In this case, tank B evidently has an adiabatic enclosure with a (small?) diathermal hole in it. This changes the equilibrium aspect of the model to be addressed, to one allowing for both mechanical and thermal equilibrium with

respect to the contents of both tanks. This also changes the conclusion reached for the resulting problem to, as Müller also states, $Q^A = 0$.

We thus believe that it is pedagogically better to treat the two cases as two different models of the situation and to compare the results of a first-law analysis of the resulting problems, rather than to present the results as two conflicting solutions of the same problem. Müller cannot on the one hand state that “tank B is adiabatic” and on the other state that there is “a heat transfer between the tanks.” Thermodynamics requires *precise*, rather than “shrewd,” statements of models and systematic analysis of resulting problems.

Concerning his “Comments on the Equation for the Uniform State, Uniform Flow Model,” we feel that Müller’s justification of his starting point for solution #1, as a consequence of a general first-law analysis for a control volume, can be strengthened. This strengthening is pedagogically important, to enable students to appreciate points at which approximations are made to exact equations.

His “generalized energy balance,” Eq. (7), should be replaced by (we also change the sign of \dot{W} , in accordance with recommended practice)

$$\frac{d}{dt} \left[m_{\text{sys}} (\tilde{u}_{\text{sys}} + \tilde{e}_{k,\text{sys}} + \tilde{e}_{p,\text{sys}}) \right] = \dot{Q} + \dot{W} + \sum_{\text{inlets}} \dot{m}(t) [\tilde{h}(t) + \tilde{e}_k(t) + \tilde{e}_p(t)] - \sum_{\text{exits}} \dot{m}(t) [\tilde{h}(t) + \tilde{e}_k(t) + \tilde{e}_p(t)] \quad (\text{A})$$

In Eq. (A), u , e_k , e_p , and h denote specific internal energy, kinetic energy, potential energy, and enthalpy, respectively, and a tilde ($\tilde{\quad}$) denotes an appropriately defined intensive

quantity. Thus, for a property within the control volume (sys)

$$\tilde{u}_{\text{sys}}(t) = \frac{U_{\text{sys}}(t)}{m_{\text{sys}}(t)} = \frac{\int_V u(\mathbf{z},t)\rho(\mathbf{z},t)dV}{\int_V \rho(\mathbf{z},t)dV} \quad (\text{B})$$

and similarly for $\tilde{e}_{k,\text{sys}}$ and $\tilde{e}_{p,\text{sys}}$. In Eq. (B), dV is a volume element, ρ is density, and \mathbf{z} denotes a point within the control volume. Correspondingly, for a property at an inlet or exit

$$\tilde{h}(t) = \frac{\dot{H}(t)}{\dot{m}(t)} = \frac{\int_A h(\mathbf{x},t)\rho(\mathbf{x},t)u_n(\mathbf{x},t)dA}{\int_A \rho(\mathbf{x},t)u_n(\mathbf{x},t)dA} \quad (\text{C})$$

and similarly for $\tilde{e}_k(t)$ and $\tilde{e}_p(t)$. In Eq. (C), dA is an area element of an inlet or exit area, \mathbf{x} denotes a point on the area, and u_n is the flow velocity normal to dA . Eqs. (A) to (C) must be supplemented with the mass-conservation equation

$$\frac{dm_{\text{sys}}}{dt} = \sum_{\text{inlets}} \dot{m}(t) - \sum_{\text{exits}} \dot{m}(t) \quad (\text{D})$$

The validity of Eq. (A) rests on two generally accepted concepts not introduced by Müller: the *continuum hypothesis* and a *local equilibrium hypothesis*. The former allows integration of point properties over volumes and areas, as in Eqs. (B) and (C), and the latter allows calculations using macroscopically based property relationships.

Equations (A) and (D) are differential equations. As in some introductory texts,^[2,3] it is tempting to deal instead with their integrated forms, between times t_1 and t_2 , say,

$$\begin{aligned} m_2(\tilde{u}_2 + \tilde{e}_{k,2} + \tilde{e}_{p,2}) - m_1(\tilde{u}_1 + \tilde{e}_{k,1} + \tilde{e}_{p,1}) \\ = Q_{12} + W_{12} + \sum_{\text{inlets}} \int_{t_1}^{t_2} \dot{m}(t) [\tilde{h}(t) + \tilde{e}_k(t) + \tilde{e}_p(t)] dt - \\ - \sum_{\text{exits}} \int_{t_1}^{t_2} \dot{m}(t) [\tilde{h}(t) + \tilde{e}_k(t) + \tilde{e}_p(t)] dt \quad (\text{E}) \end{aligned}$$

$$m_2 - m_1 = \sum_{\text{inlets}} m_i - \sum_{\text{exits}} m_e \quad (\text{F})$$

Equations {(A),(D)} and {(E),(F)} are exact. Equation (E) is only a *formal* result and may not always be useful, however. This form is deceiving since it implies neglect of any interdependence of the left and right sides of Eq. (A).

Simplification of Eqs. {(A),(D)} or {(E),(F)} involves invoking appropriate approximations for special cases of the spatial and temporal dependence of the properties at the inlets and exits and of the system. Important special cases are

- *uniform flow*, for which the properties *at an inlet or exit* are independent of position \mathbf{x} (giving $\tilde{h}(t) \equiv h(t)$) (or for each phase of the flow)
- *uniform state*, for which the properties *of the system* are independent of position \mathbf{z} (giving $\tilde{u}_{\text{sys}}(t) \equiv u_{\text{sys}}(t)$) (or for each phase within the system)
- *steady-property flow*, for which the properties *at an inlet or exit* are independent of time t
- *steady flow*, for which \dot{m} *at an inlet or exit* is independent of time t (steady flow usually implies steady-property flow, but the converse is not necessarily true)
- *steady state*, for which the properties *of the system* are independent of time t ; this entails the vanishing of the left side of Eq. (A) (steady state usually implies steady flow and steady-property flow)

The uniform flow (UF) assumption at inlets and exits (incorporated without comment by Müller in his Eq. 7) and the uniform state (US) assumption for the system are often used in the absence of any information concerning spatial dependence of the properties. (The former is consistent with a plug-flow assumption and the latter with a well-stirred vessel assumption.) Together, they form part of the basis for an unsteady-state flow model referred to by Müller as the "Uniform-State Uniform-Flow (USUF) model." This designation by itself is misleading, however, since this model includes a third assumption that corresponds to the steady-property flow assumption defined above. As essentially pointed out by Müller, these three assumptions (together with neglect of kinetic and potential energy terms) allow Eq. (E) to be simplified to Müller's Eq. (1), his "working equation" of the USUF model.

More generally, for unsteady-state flow processes, the steady-property flow assumption does not hold, and the USUF model is invalid. We do not believe that it should be emphasized pedagogically since it severely restricts the first-law analysis to rather special cases, such as the discharge situation described by Müller in his solution #1 and filling a vessel from a constant-property source/reservoir. We recommend instead that a first-law analysis deal directly with the differential equations (A) and (D) as such. This approach handles all situations (including the USUF model as a special case), and is consistent with the approach of some introductory texts^[4,5] and recent pedagogical articles.^[6,7]

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References

1. Müller, E.A., "A Thermodynamics Problem with Two Conflicting Solutions," *Chem. Eng. Ed.*, **34**(4), 366 (2000)

- Sonntag, R.E., C. Borgnakke, and G.J. van Wylen, *Fundamentals of Thermodynamics*, 5th ed., Wiley, New York, NY, pp. 163-173 (1998)
- Çengel, Y.A., and M.A. Boles, *Thermodynamics*, 3rd ed., McGraw-Hill, New York, NY, pp. 222-229 (1998)
- Elliott, J.R., and C.T. Lira, *Introductory Chemical Engineering Thermodynamics*, Prentice-Hall PTR, Upper Saddle River, NJ, pp. 72-77 (1999)
- Sandler, S.I., *Chemical and Engineering Thermodynamics*, 3rd ed., Wiley, New York, NY, pp. 30-36 (1999)
- Wisniak, J., "Discharge of Vessels: Thermodynamic Analysis," *J. Chem. Ed.*, **74**, 301 (1997)
- de Nevers, N., "Non-Adiabatic Container Filling and Emptying," *Chem. Eng. Ed.*, **33**, 26 (1999) □

To The Editor:

In the Fall 2000 Class and Home Problems Column, E.A. Müller^[1] proposes a thermodynamics problem designed to demonstrate that two seemingly correct but incompatible solutions can be found from the thermodynamic analysis of a particular process, and furthermore that such incompatible solutions provide an opportunity to improve one's understanding of thermodynamic analysis.

Müller proposes the following: Consider two tanks, A and B, connected with a valve and initially filled with (ideal) gas at the same temperature, but the pressure in A is greater than the pressure in B. Tank B is well insulated (adiabatic), but tank A is maintained at constant temperature by thermal contact with a heat source or sink.

Müller asks: "If the valve that connects both tanks is opened and equilibrium is attained, will it have been necessary to add (or to remove) heat from tank A?" (Denoted as Q^A .)

For this problem, it is clear that tanks A and B will be at the same pressure at the end of the process. But Müller clearly intends that tanks A and B are also at the same temperature when equilibrium is attained. For tanks A and B to reach the same temperature at equilibrium would require that tanks A and B be in thermal contact. Clearly, the contradiction is that tank B cannot be well insulated (adiabatic) and in thermal contact with tank A. This contradiction appears in both solutions presented in the paper.

Solution #1 is obtained by considering an energy balance on a control volume around tank A and shows that $Q^A > 0$. Müller subsequently argues that this solution is incorrect by considering an energy balance on a control volume around tank B; for this system, the paper (correctly) shows that energy must be removed from tank B if the temperature of tank B is unchanged. Since Müller is treating the temperature of tank B to be the same as tank A (and the temperature of tank A is unchanged), energy must be removed from tank B, which violates the requirement that tank B be adiabatic.

In fact, since tank B is well insulated, the energy balance on tank B in the paper correctly shows that the temperature in tank B will increase at equilibrium.

Solution #2 is obtained by considering an energy balance on a control volume around both tanks and the connecting piping, so that the change in internal energy must equal the heat transfer to tank A (Q^A). Since Müller intends the temperatures in the two tanks to be equal at equilibrium, the internal energy is unchanged, and $Q^A = 0$. As discussed earlier, the temperature in tank B actually increases during the process, so the internal energy of the system increases, and $A^A > 0$.

Another way to show $Q^A \neq 0$ is to consider a system such as the contents of tank A after equilibrium is attained. Now, suppose $Q^A = 0$. The contents of such a system could then be considered to undergo an adiabatic reversible expansion (since $Q^A = 0$). Note however that $(\partial T/\partial P)_S > 0$ for all gases (real and ideal). Therefore, when the pressure in tank A decreases, the temperature in tank A also decreases—but this is a contradiction since tank A must be maintained at a constant temperature. Therefore, Q^A cannot equal 0.

Irrespective of the difficulties expressed above, Müller's point is well made that one's understanding is improved by resolving the dispute between seemingly incompatible thermodynamic analyses.

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Reference

- Müller, E.A., "A Thermodynamics Problem with Two Conflicting Solutions," *Chem. Eng. Ed.*, **34**(4), 366 (2000)

Author's Response to Letters to the Editor

I have received many comments, personally and publicly, on the problem I presented in the Fall 2000 issue of *CEE*. As with Levenspiel's original thermo problem, each and every comment is different, ranging from "You chose the wrong answer" to "Send me another one of these problems."

The main message of the paper is that if you use equations straight out of a book and apply them to a problem without fully understanding the assumptions behind the equations, you have a chance of coming to a false conclusion. Nevertheless, I think some readers "missed the point," and I believe further discussion is in order.

The initial problem is clearly stated, especially with regard to the final state: "equilibrium is attained." In a simple system such as this, thermodynamic equilibrium requires the

simultaneous achievement of three conditions: homogeneity of pressures (mechanical equilibrium), homogeneity of temperature (thermal equilibrium), and homogeneity in chemical potential (diffusive equilibrium); i.e., *only* if all three conditions ($P^A = P^B$, $T^A = T^B$, and $\mu^A = \mu^B$) are simultaneously met can we affirm that the system will not change in time if left alone.

Solution #1, as Missen and Smith note, pertains to the achievement of mechanical equilibria, but as is also noted in the original article, leaves a temperature gradient among tanks A and B. Given enough time, mass diffusion must take place, transferring *energy* from tank B to tank A. So, even though tank B has adiabatic walls and thus no heat transfer to the surroundings, it does transfer energy due to a temperature difference.

In hindsight, the phrase "Given enough time, this temperature gradient will produce a transfer between the tanks" should read, "Given enough time, this temperature gradient will produce a mass transfer and consequent energy transfer between the tanks" in order to be unambiguous.

It is clear, however, that there are not two solutions to the problem, even if the catchy title implies so. Only one solu-

tion is possible. Any argument attempting to set solution #1 as the correct one must first disprove solution #2—an impossible task.

Many students and teachers (and Spicer's note is a clear example) apply the textbook equations directly to a problem without further thought on the problem. It is in this sense that I totally agree with the second point noted by Missen and Smith. I believe that one should teach the general energy balance, and for each particular case simplify it accordingly.

The point of the original class problem is that if one starts directly with Eq. (2), one may elude some of the assumptions behind its derivation. One should always start with a generalized equation such as Eq. (7)* and integrate it according to the given problem. Categorizing systems as steady state, uniform flow, etc., and stating formal equations in each case only entices the student to learn a myriad of equations, making things more difficult and prone to errors.

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* Equation (7) is identical (with the exception of the arbitrary sign given to the work) to Eq. (A) of Missen and Smith, not to Eq. (E) as stated in their comment.

ChE book review

Advanced Transport Phenomena

by John C. Slattery

Published by Cambridge University Press, The Edinburgh Building, Cambridge, UK; 734 pages; available in paperback and hardcover

Reviewed by

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Advanced Transport Phenomena is a new textbook written by Professor J.C. Slattery that represents a revision of an earlier text by the same author: *Momentum, Energy and Mass Transfer in Continua* (1981). Transport phenomena is a fascinating and interdisciplinary subject that is covered by at least one required course in all graduate chemical engineering programs and remains an active area of research. Like its predecessor, the new book is intended for graduate students in engineering.

The text is organized into three topics according to the main subjects of transport phenomena: momentum, energy, and mass transfer. In addition, there are two shorter topics that are covered; kinematics (coming before the three main topics) and tensor analysis (an appendix). Each of the three main topics is divided into three sub-topics that can roughly

be described as the formulation, application, and reduction of transport balance equations. This matrix style of organization, where the columns are the main topics (momentum, heat, and mass) of transport phenomena and the rows provide the components and applications for each topic, is similar to that used in the classic text *Transport Phenomena* by Bird, Stewart, and Lightfoot (BSL), and allows the instructor/reader the flexibility to cover the topics by column or by row.

The style and teaching philosophy of the author are revealed in Chapter 1 (kinematics) where concepts such as motion, velocity, and phase interfaces are introduced. Various transport theorems are developed and used to derive the differential mass balance, or continuity equation, and the jump mass balance from the mass conservation postulate. Hence, the approach taken here and throughout the book is to start from general postulates about the physical world and to convert these postulates into useful conservation equations using formal mathematical tools.

The sub-topic structure is itself instructional in that the reader is forced to recognize the similarities (and differences) between momentum, heat, and mass transfer. In Chapters 2, 5, and 8 (Foundations for...), differential forms of the conservation equations and their corresponding two-dimensional forms (jump balances) are derived simultaneously.