

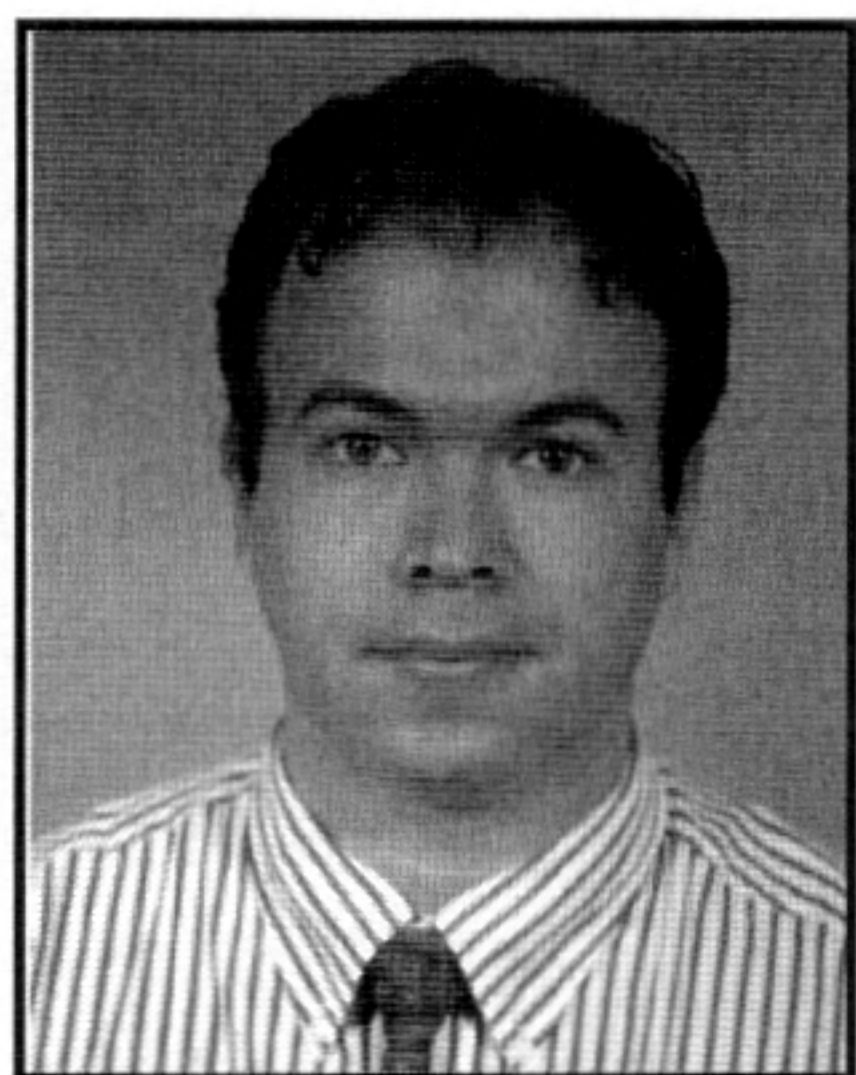
The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed ten double-spaced pages if possible and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@engin.umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

A THERMODYNAMICS PROBLEM WITH TWO CONFLICTING SOLUTIONS

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A thermodynamics course is particularly prone to difficulties, both in teaching and in learning, probably because in most curricula it corresponds to one of the first engineering courses in which it is not only necessary to master the physics of the problem and the governing equations, but also requires common sense to use them appropriately. In a recent paper,^[1] Levenspiel showed how a properly (or should we say “shrewdly”) stated thermodynamics problem can be used to point out deficiencies in the use and teaching of certain concepts. Another of these examples is presented here. It is an analog of “typical” textbook problems^[2,3] and apparently has two conflicting solutions.



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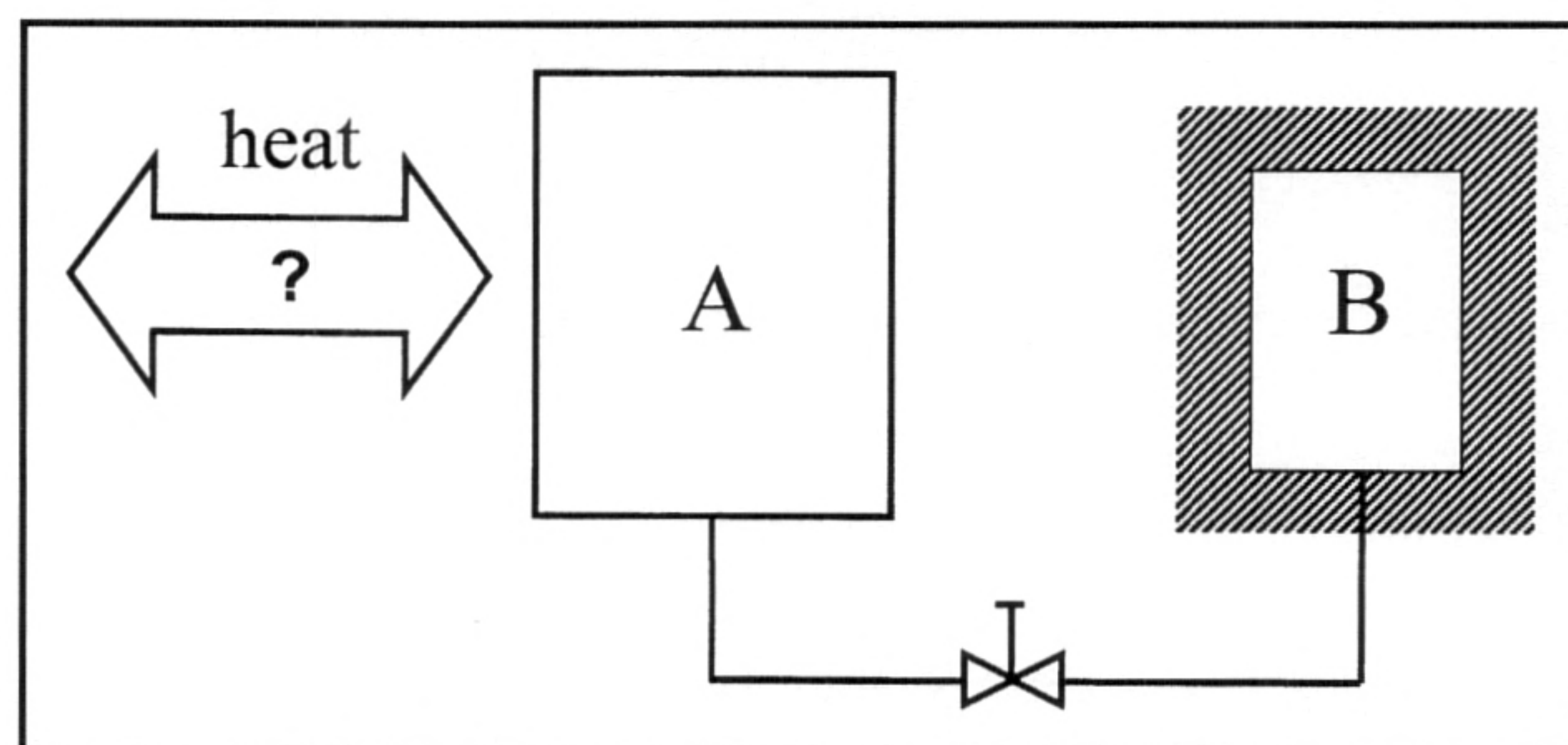


Figure 1.

PROBLEM

Consider two tanks, A and B, as shown in Figure 1. Both are initially filled with the same gas, which for practical purposes may be considered ideal. Initially, both tanks are at the same temperature, T , but tank A is at a greater pressure than tank B and is always kept at constant temperature by means of heat transfer to the surroundings. On the other hand, tank B is adiabatic. 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?

The problem may also be stated quantitatively by giving numerical values to the initial temperature, pressures, and volumes. The problem may even be extended by asking for

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an entropy and/or an availability balance. In any case, two (and maybe more) solutions are readily found.

SOLUTION #1

If one takes A as the system, one can apply the uniform state approximation,*

$$Q^A = (m_2^A u_2^A - m_1^A u_1^A) + m_e^A h_e \quad (2)$$

The ideal gas model holds, so the energies and enthalpies can be substituted for their corresponding expressions** ($u=C_v T$; $h=C_p T$). Since the temperatures do not change, the enthalpy of the exiting fluid is constant and proportional to the system temperature; thus

$$Q^A - [(m_2^A - m_1^A)C_v + m_e^A C_p]T = m_e^A (C_p - C_v)T = m_e^A RT \quad (3)$$

Mass must be interchanged (due to the initial pressure difference), and the mass exiting the tank A, $m_e^A = (m_1^A - m_2^A)$, is a positive quantity. Since the RT term is also positive, one concludes that $Q^A > 0$.

SOLUTION #2

If one considers both tanks and the valve as the system, one may apply the first law to the closed system and obtain

$$Q = \Delta U + W \quad (4)$$

Since B is adiabatic, $Q(=Q^A)$ will refer to the heat exchanged by A. The system produces no work ($W=0$), and in the final equilibrium state, the gas in both A and B will be at temperature T (since A is isothermal). For an ideal gas with no

* The uniform state, uniform flow process is an unsteady state in which the mass that crosses the control surface has constant thermodynamic properties. This allows an integrated first-law expression

$$Q + \sum m_i h_i = (m_2 u_2 - m_1 u_1) + \sum m_e h_e + W \quad (1)$$

where “i” and “e” refer to incoming and exiting streams, respectively, and 1 and 2 refer to the initial and final states. Q is the heat added to the system. W is the work done by the system, and m is mass. This equation is discussed in detail at the end of this article.

** With the implicit assumption that a reference state is taken as $u=0$ at $T=0$. This fact is, however, irrelevant to the solution, since the heat capacities factor out.

*** Remember that for an ideal gas, the energy is only a function of the temperature. In fact, the enthalpy $h=u+Pv$ is also a function of only the temperature since $Pv=RT$. For real gases, this is no longer true.

temperature change, there is no change in internal energy*** ($\Delta U=mC_v T=0$) and therefore one concludes that $Q^A=0$.

Both solutions are obviously conflicting, but they both seem to follow the “standard textbook resolutions.” What went wrong?

Comment on the “Conflicting” Solutions

Solution #2 is the correct answer. Unfortunately, Solution #1 is obtained by straightforward application of standard control-volume equations as taught in classical textbooks. In fact, there is nothing wrong with the development of solution #1. It is, however, incomplete. If we were to take a control volume on tank B (the valve is isenthalpic and therefore irrelevant), one finds that

$$Q^B = m_i^B h_i = m_2^B u_2^B - m_1^B u_1^B \quad (5)$$

$$Q^B = (m_2^B C_v T - m_1^B C_v T) - m_i^B C_p T = m_i^B C_v T - m_i^B C_p T = -m_i^B RT \quad (6)$$

i.e., $Q^B < 0$! But, this is in contradiction to the problem statement. Since no heat transfer to the surroundings is allowed, to maintain the final temperature of the whole system at T, energy must leave tank B in an amount (not surprisingly) equal to $m_i^B RT (=m_e^A RT)$. This energy will leave tank B and enter tank A. Therefore, the *net* energy transfer to the surroundings is zero. If the opening of the valve were sudden, the most likely outcome of the system is that the pressures would equate rather rapidly due to the corresponding mass transfer.

At this point, A will have decreased its temperature due to adiabatic decompression, while B will have increased its temperature due to an adiabatic compression. Given enough time, this temperature gradient will produce a heat transfer between the tanks. The final resulting temperature equilibrium temperature is T, requiring no external heat transfer. Solution #1 is giving us only the half-time solution. In fact, it does not take into account the final condition on the temperature of tank B. The “trick” of the question is the phrase “until equilibrium is attained” at the end of the problem statement, since one could note that mechanical equilibrium (equal pressures) does not imply thermal equilibrium.

The system is analogous to Joule's experiment (see Figure 2) in which two tanks, one containing an ideal gas and the other is evacuated, are put in contact by opening the valve in the pipe joining them. The pressure in both tanks is equated, but no temperature change is observed experimentally. (This experiment is used to demonstrate how the internal energy of ideal gases is a function only of their temperature, since both heat and work are zero.)

Another interesting analog to the problem (see Figure 3) is that of a single tank with an internal diathermic partition where part of the system has adiabatic walls. At a given moment the partition is eliminated and the system attains a final homogeneous state. Notice how, in this analogy, the adiabatic walls of B are irrelevant to the problem.

Comments on the Equation for the Uniform State, Uniform Flow Model

At the start of Solution #1, a version of the first law for uniform state is invoked. In order to obtain such an equation, one must start with a generalized energy balance (first-law equation for an open system)

$$\dot{Q} + \sum_{\text{inlet}} \dot{m} \left(h + \frac{1}{2} \text{vel}^2 + gz \right) = \frac{dE}{dt} + \sum_{\text{exit}} \dot{m} \left(h + \frac{1}{2} \text{vel}^2 + gz \right) + \dot{W} \quad (7)$$

and integrate with respect to a time differential each element of the equation. For some instances this is straightforward, e.g.,

$$\int_1^2 \dot{Q} dt = \int_1^2 \frac{dQ}{dt} dt = \int_1^2 dQ = Q \quad (8)$$

but for the terms associated with the mass flow, a problem arises: in principle, both the mass flow and the thermodynamic properties of the system may vary with time, which brings the dilemma that we must then attempt to evaluate integrals of the type

$$\int_1^2 \dot{m}(t) x(t) dt \quad \text{where } x(t) \text{ may be } h, \frac{1}{2} \text{vel}^2, \text{ or } gz \quad (9)$$

These integrals may only be evaluated for the (unusual) case in which the functionalities with time are known explicitly or for the case in which either (or both) \dot{m} and x are constant. In a general case, one makes the following assumption:

Assumption #1: "The properties of the mass entering or leaving the control volume are constant." With this,

$$\int_1^2 \dot{m}(t) x dt = x \int_1^2 \dot{m}(t) dt = xm \quad (10)$$

but if the velocity and the thermodynamic properties are constant, then how can the mass flow *not* be constant?

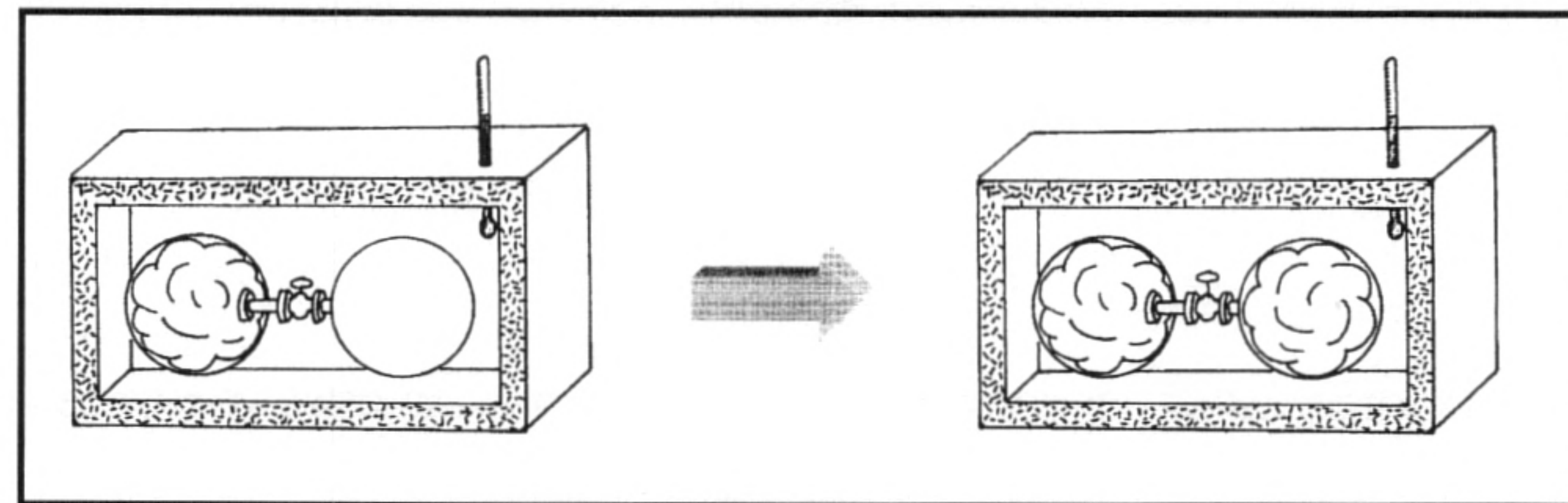


Figure 2

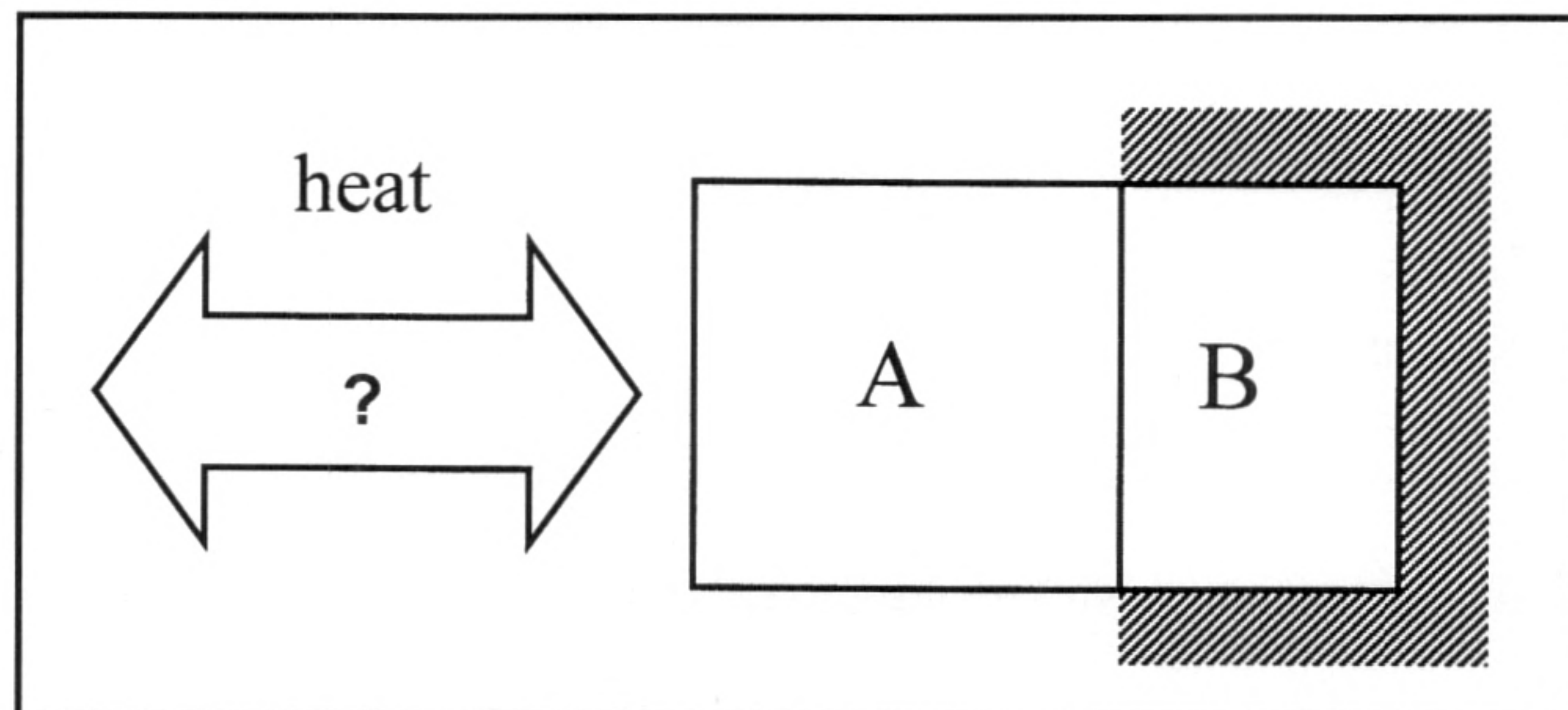


Figure 3

$$\dot{m} = \frac{m}{t} = \frac{m}{V} \frac{V}{t} = \rho \frac{L}{t} A = \rho \text{vel} A \quad (11)$$

in which A is the area for flow. This confusion can be avoided if we make an additional assumption for the uniform state:

Assumption #2: "The kinetic and potential energy changes are negligible compared to changes in internal energy," which is generally true. The final assumption in the model is:

Assumption #3: "The system can be defined by a unique thermodynamic state (therefore uniform state)." Thus, the energy accumulation term can also be integrated as

$$\int_1^2 \frac{dE}{dt} dt = \int_1^2 \frac{dU}{dt} dt = \int_1^2 dU = U_2 - U_1 = m_2 u_2 - m_1 u_1 \quad (12)$$

The final "working equation" for the Uniform State, Uniform Flow (USUF) model is then

$$Q + \sum m_i h_i = (m_2 u_2 - m_1 u_1) + \sum m_e h_e + W \quad (1)$$

Some textbooks^[3] do not make assumption #2 clear, while others^[2,4] (wisely?) do not present the uniform state as a distinct model, preferring to categorize the open systems as either steady state or unsteady state (transient).

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