has been pointed out that the interplay between instructor and student is enhanced in such a course when a sound basis for communication exists between them. The problems associated with establishing a laboratory facility consistent with the instructional level have been outlined and a workable scheme suggested. A syllabus drawn from one of the standard texts has been described, and a number of variations and pedagogical techniques found to be successful in the author's presentation of the course have been outlined. Typical objectives that one might realistically hope to achieve in a course of this kind have been set forth and a student body capable of realizing these objectives noted. Finally, the suitability of this course for presentation by chemical engineering faculty members has been pointed out with suggestions for course development and staffing.

The author welcomes questions and comments from those interested in such a program or already involved in its presentation.

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ChE problems for teachers

DOES THE ENTROPY OF A COMPOUND SYSTEM ALWAYS MAXIMIZE IN THE EQUILIBRIUM STATE?

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This provocative paper elicited considerable interest when presented at a recent AIChE meeting. CEE publishes it with the expectation that it will stimulate discussion and response from our readers.

IT IS CONVENTIONAL in thermodynamics to introduce two different types of walls which are impermeable to matter — adiabatic and diathermal. An adiabatic wall is used in introducing the first law of thermodynamics and also is required in developing the concept of isolation. In the strictest sense, no real material does form an adiabatic enclosure, but rather approximates one to varying degrees. A Dewar flash is a well-known example of an enclosure that approximates adiabatic behavior to a very high degree. A diathermal wall is used in the statement of the "zeroth" law, the condition of thermal equilibrium.

Excellent discussions of the properties of both types of walls are available[1–3]. It is not the purpose of this paper to improve on those discussions. Rather its purpose is to point out a fact which is felt to be too little appreciated in applications of the subject — the presence of an adiabatic wall constitutes a constraint on equilibrium. The following question will bring this last statement into sharp focus. **Do examples exist of systems which can be treated using classical thermodynamics for one type of wall (i.e. diathermal) and not the other?**

The answer to this question is yes, and the particular example chosen causes one to recognize the great importance of a careful statement of the entropy maximum principle. The paper will show that the principle as commonly stated does NOT always apply to the prediction of the squilibrium state.

STATEMENT OF THE PROBLEM

CONSIDER A COMPOUND system composed of two subsystems which are simple compressible fluids. The subsystems are each in equilibrium states and are separated by an adiabatic wall. The wall is pinned in a fixed position initially and the properties of the subsystems are given by P_1', V_1', T_1', P_1'', V_1'', and T_1''. The subscript refers to the state of the system and the superscript is used to differentiate between subsystems. Figure 1 is a schematic representation of the system.

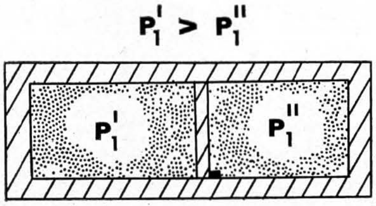

Fig. 1. — Schematic Representation of the Compound System.

Both subsystems are enclosed totally within adiabatic walls. For all cases considered in this paper different initial pressures, $P_1' > P_1''$ are assumed. As described, the compound system is subject both to a mechanical constraint, the pinned wall, and a thermal constraint, the adiabatic wall. The mechanical constraint, the constraint on the initial position of the wall, is removed, and the wall (assumed to be frictionless) will oscillate a number of times, but will eventually come to rest in another equilibrium position. At that time the subsystems will satisfy the condition of mechanical equilibrium

$$P_2' = P_2'' \qquad (1)$$

Can the other parameters of state, V_2', T_2', V_2'', and T_2'' be predicted? That question has been discussed[4–6] and the answer is negative. If the dividing wall is a diathermal one, however, the entropy maximum principle may be employed to yield the additional condition

$$T_2' = T_2'' \qquad (2)$$

This together with an equation of state

$$V = V(P,T) \qquad (3)$$

for each of the subsystems, will be sufficient to determine the parameters of the final equilibrium state. Equation (2) holds with a diathermal separating wall as this wall does not constrain the establishment of thermal equilibrium.

These findings can be summarized in the following manner: the ability of classical thermodynamics to analyze a compound system which clearly starts and ends in equilibrium states is dependent on the choice of the dividing wall. The analysis is possible for a diathermal wall but is not possible for an adiabatic dividing wall. This fact has been recognized and careful statements of the entropy maximum principle[7–9] make direct reference to it.

The remainder of this paper will be devoted to an elaboration of the limits of thermodynamics in predicting the parameters of state of a system in constrained equilibrium.

ANALYSIS

ATTENTION IS ONCE again directed to the example introduced earlier, the compound system with an internal adiabatic wall. For simplicity all analyses are limited to subsystems which are monatomic ideal gases. If more realistic equations of state were employed, more involved arguments would be necessary. The ability to predict the final equilibrium state does not depend upon the functional form of the equation of state, in any event.

The second law written for the changes of state for each of the subsystems yields,

$$\triangle S' = S_2' - S_1' \geq 0 \qquad (4)$$

$$\triangle S'' = S_2'' - S_1'' \geq 0 \qquad (5)$$

for the change of state from the initial equilibrium state, state 1, to the final equilibrium state, state 2, under adiabatic constraints. The author has shown[4] that only the inequalities given in equations (4) and (5) can hold in this case. The subsystems do not experience quasi-static adiabatic changes of state. This result, which is almost obvious, will be of importance to us in our subsequent analyses.

Suppose, for example, one assumes that while the entropy of the compound system does not maximize, the subsystems do attain states which yield the maximum entropy for the compound system subject to the adiabatic constraints. This state is designated as state 2*. Figure 2 is a representation of the equilibrium states of the compound system. State 2* is the final equilibrium state with maximum entropy which results with an adiabatic dividing wall. State e is the equilibrium state which would result with a diathermal dividing wall.

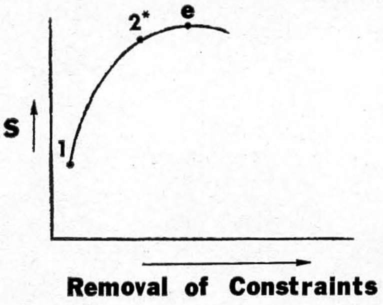

Fig. 2. — Equilibrium States of the Compound System.

In general, states 2* and e do not coincide. In addition, it can be shown that in general the subsystems do not attain equilibrium states which maximize the entropy of the compound system. The compound system cannot reach state 2* either. The following will establish this last point.

CONSIDER THE CASE where the initial states of the two subsystems have the values given in Table 1.

TABLE 1. Initial Equilibrium States of the Subsystems

	Subsystem prime	Subsystem double prime
Pressure, psia	500	100
Temperature, °R	1000	600
Volume, cu. ft.	8	8

These conditions are sufficient to set the pressure of state 2, when both subsystems are monatomic ideal gases, which can be calculated to be $P_2' = P_2'' = 300$ psia.

In order to evaluate the change in any other thermodynamic property, a second parameter of state must be given. As pointed out earlier, this parameter is not known. The entropy change of each of the subsystems can be evaluated however from the known value of P_2' and from assumed values of V_2'. Equations (6) and (7) can then be employed to evaluate $\Delta S'$ and $\Delta S''$.

$$\Delta S' = n' R \left[\frac{5}{2} \ln \frac{V_2'}{V_1'} + \frac{3}{2} \ln \frac{P_2}{P_1'} \right] \tag{6}$$

$$\Delta S'' = n'' R \left[\frac{5}{2} \ln \frac{V_2''}{V_1''} + \frac{3}{2} \ln \frac{P_2''}{P_1''} \right] \cdot \tag{7}$$

Various V_2' values were assumed and used along with the values of the other variables given in equations (6) and (7) to determine the results given in Table 2.

TABLE 2. Dependence of Entropy Changes of Assumed Values of V_2'

V_2' assumed cu. ft	$\Delta S'$ e.u.	$\Delta S''$ e.u.	$\Delta S' + \Delta S''$ e.u.
7.0	−4.400	+2.590	−1.810
8.0	−3.065	+2.197	−0.868
9.0	−1.887	+1.752	−0.135
10.0	−0.834	+1.238	+0.404
11.0	+0.120	+0.630	+0.750
12.0	+0.990	−0.113	+0.977
13.0	+1.790	−1.072	+0.718
14.0	+2.531	−2.424	+0.107

The reader will recall that only those states where $\Delta S'$ and $\Delta S''$ are > 0 can be realized. Figure 3 has been prepared using the range of values of V_2' where both $\Delta S'$ and $\Delta S''$ are > 0.

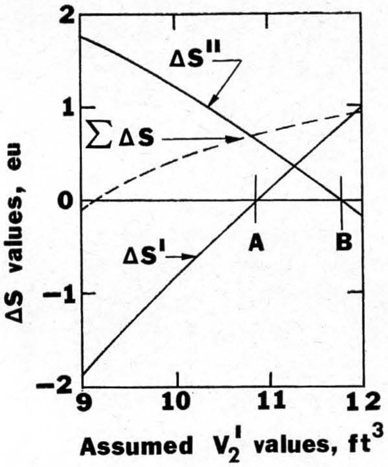

Fig. 3 — Entropy Changes vs. Assumed Final Volumes.

From Figure 3 it is seen that the range of possible V_2' values must be in the zone indicated (between points A and B in Figure 3). The sum of $\Delta S'$ and $\Delta S''$ is also plotted as the dotted line on this Figure. By inspection of either Table 2 or Figure 3, it is seen that the maximum of the sum of $\Delta S'$ and $\Delta S''$ occurs at a V_2' value of 12, and that $\Delta S''$ is < 0 for this value. The state with a V_2' value of 12 corresponds to state e in Figure 2. Clearly the compound system cannot attain this state when subject to the thermal constraint of the adiabatic wall. The point of immediate interest is to demonstrate that the compound system cannot attain state 2^* either.

Inspection of Table 2 and Figure 3 reveals that the state where $\Delta S = 0$ corresponds to state 2^* in Figure 2. Over the range of possible V_2' values ($A \leq V_2' \leq B$) the function $\Delta S' + \Delta S''$ is monotonically increasing and it reaches its maximum value where $\Delta S'' = 0$. It was shown earlier, however that both $\Delta S'$ and $\Delta S''$ must be > 0 when separated by an adiabatic wall, and so the possibility of the compound system ever attaining this state can be dismissed. In short, for the initial conditions selected, the entropy of the compound system did not maximize in the presence of an internal adiabatic constraint. The compound system was not able to reach state 2^*. An infinity of initial states having this property exist. The author has shown[4], however, that another infinity of initial states also exist for which we may not make that statement. There are initial states for which we may not exclude the compound system from attaining the state of maximum entropy. One such state is to use the initial pressures and temperatures given in Table 1 but to let $V_1' = 2$ cu. ft. and $V_1'' = 14$ cu. ft. This set of initial conditions will give equilibrium values whereby both $\Delta S'$ and $\Delta S''$ are > 0 *even* with a diathermal separating wall.

What statement can be made concerning the final equilibrium state of the compound system shown in Figure 1? Certainly the entropy of the compound system does increase when the mechanical constraint is removed. In general, however, the entropy does not reach its global maximum (state e) nor does the compound system maximize the entropy subject to the adiabatic constraint (state 2^*). Just how much the entropy does increase cannot at present be determined by the tools of classical thermodynamics.

CONCLUSIONS

The key point in our discussion has been the following — the presence of an adiabatic internal wall represents a constraint on thermal equilibrium and a system in constrained equilibrium need NOT be in the state of maximum entropy. Thus the characteristics of the dividing wall, which may at first appear to be an unimportant element, are critical for the prediction of the final equilibrium state.

NOTATION

n — number of moles, lb. moles
p — pressure, psia
R — ideal gas constant, psia-ft^3/lb mole — °R
S — entropy, e.u.
T — absolute temperature, °R
V — volume, cu. ft.
Δ — refers to change in value of a thermodynamic property

Subscripts

1, 2 refer to equilibrium state with adiabatic separating wall

Superscripts

prime, double prime — used to designate subsystems

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BOOK REVIEW

(Continued from page 61)

very much time left for other university work during the senior year.

This report should be of value to teachers of chemical engineering design who are willing to bite off a rather formidable chunk of a large and involved process. Some pitfalls are that naphtha is not a representative feedstock for U. S. ethylene manufacture, that the economics must be adapted to U. S. circumstances, and that the information is only that which has been gleaned from the open literature. The counsel of practitioners engaged in the ethylene business would be advisable. Perhaps the best use of the report would be in providing material for short design studies. Example sections amenable to adaptation would be cracked gas drying, acid gas sweetening, and acetylene removal by hydronation.

In summary, this is a collection of design problem solutions that in whole, or in part, can be of value to the teacher of chemical engineering design. *Reviewed by Dr. James R. Fair, Monsanto Company, St. Louis, Mo.*

Continued on page 97)