ChE problems for teachers

Professor R. R. Davidson of Texas A&M University comments on Professor A. J. Brainard's problem in the Spring issue of **CEE.**

After hearing Dr. Brainard's talk "Does the Entropy of a Compound System Always Reach Its Maximum?" at the February meeting of the AIChE in Atlanta, I gave my graduate thermo class a quiz containing the following pair of questions:

1. Given the first and second law and that internal energy and entropy are state functions, show that for any process in an adiabatically isolated system $\triangle S \geq 0$.

2. Given a system comprised of two chambers separated by a freely moving adiabatic wall or piston. The entire system and each chamber is adiabatic. Both chambers contain gases, but the pressure is higher in Chamber I and the piston is kept from moving by a stop (Brainard's Figure 1). If the stop is removed so that the piston can move freely until it comes to rest with the pressures in the chamber equalized, will the change in entropy be less than, equal to, or greater than zero in

(a) The entire system

(b) Chamber I

(c) Chamber II

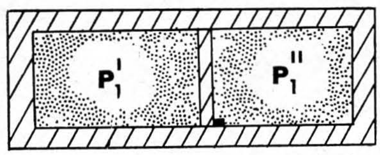
(d) Is the entropy of the entire system necessarily at a maximum?

The answer to (a), (b), and (c) follows directly from the results of Problem 1. Since the initial pressures in Chambers I and II were unequal, the process was irreversible, and since the entire system as well as Chambers I and II were each an adiabatically isolated system, the entropy change in each case was greater than zero.

The answer to Problem (d) is no, because the maximum entropy is reached when thermodynamic equilibrium is reached and this system is not necessarily in thermodynamic equilibrium because the temperatures in the two chambers are not necessarily equal. The word necessarily is used because one might, by manipulating the initial temperatures, obtain a final state in which the temperatures are equal.

The final state in this problem cannot be obtained by thermodynamics. Given the weight of the piston, its coefficient of friction, the dampening factor for the gas and its PVT properties, the final position of the piston could be calculated, but this is a problem in mechanics,

$P_1^{I} > P_1^{II}$



not thermodynamics. Thermodynamics can only say that the final entropy is greater than the initial value and less than the value that could be calculated if heat could flow freely through the piston giving a uniform temperature throughout the system.

I think it should be stressed that our inability to obtain a thermodynamic solution for the final adiabatic state is not due to a lack of thermodynamic rigor, but to the fact that the solution does not lie within the realm of thermodynamics. In general thermodynamics can only give answers for equilibrium states and this means, among other things, that the temperature is uniform throughout the system.

After the quiz a student posed a good question.

What if different gases were on each side of the piston, wouldn't we have to let the gases mix before thermodynamic equilibrium could be obtained?

The answer is yes and no. It is true that if we punched a hole in the piston the entropy would further increase. While we might consider this final state to be the global maximum of the entropy, the final state without mixing, but at uniform temperature, is a local maximum having a thermodynamic solution. It is unlike the state in which only mechanical equilibrium is reached for which there is no thermodynamic solution at all.

The system at uniform temperature is at a definite state before and after the hole is punched in the piston, and so the entropy of adiabatic mixing can be thermodynamically calculated. However, with the adiabatic piston, the final temperatures are undefined because the internal energy of the total system, though known and constant, can be distributed in an infinite number of ways. Thus we see that imposing an impermeable wall is not like imposing an adiabatic wall.

It was interesting to note that while many students missed part (d), a number also missed part (b) and (c). They seemed intuitively to want to conserve entropy, and they found it hard to believe that it increased on both sides of the piston even though they had just proved it in Problem 1.