10.40 Thermodynamics **Fall 2003**
Problem Set 5

Problem #2

Rocky and Rochelle are having one of their classic arguments regarding thermodynamics and they need your help. Imagine a process where supercritical CO2 gas at 320 K and 100 bar is added to a cylinder while maintaining the total entropy and pressure constant. Rocky says that the temperature will increase and Rochelle says it will decrease. Who is correct? Is it possible that they both could be correct? You may want to start your analysis by developing an expression for the temperature change per mole of component j added to a multicomponent mixture under conditions of constant S, P and Ni [j]. Relevant property data are given at the end of the problem.

Solution:
This problem is asking us to evaluate the following derivative:

$$\left(\frac{\partial T}{\partial N_j}\right)_{\underline{S},\,P,\,N_{i[j]}} \tag{1}$$

To start, we use the triple product rule with respect to S to remove it from the list of variables held constant:

$$\left(\frac{\partial T}{\partial N_j}\right)_{\underline{S},\,P,\,N_{i[j]}}\left(\frac{\partial N_j}{\partial \underline{S}}\right)_{T,\,P,\,N_{i[j]}}\left(\frac{\partial \underline{S}}{\partial T}\right)_{N,\,P} = -1 \tag{2}$$

$$\left(\frac{\partial T}{\partial N_j}\right)_{\underline{S},\,P,\,N_{i[j]}} = \frac{-\left(\partial \underline{S}/\partial N_j\right)_{T,\,P,\,N_{i[j]}}}{\left(\partial \underline{S}/\partial T\right)_{N,\,P}} \tag{3}$$

We now simplify the numerator and denominator of equation (3):

$$\left(\frac{\partial \underline{S}}{\partial T}\right)_{N,\,P} = N\left(\frac{\partial S}{\partial T}\right)_{N,\,P} = N\frac{C_P}{T} \tag{4}$$

$$\left(\frac{\partial \underline{S}}{\partial N_j}\right)_{T,\,P,\,N_{i[j]}} = \bar{S}_i = S \text{ for a one component system} \tag{5}$$

Equation (5) is true because for a one component system:

$$\left(\frac{\partial \underline{S}}{\partial N}\right)_{T,\,P} = \left(\frac{\partial NS}{\partial N}\right)_{T,\,P} = N\underbrace{\left(\frac{\partial S}{\partial N}\right)_{T,\,P}}_{=0 \text{ by Eq. 5.19 in text. Only n+1 independent intensive variables}} + S\underbrace{\left(\frac{\partial N}{\partial N}\right)_{T,\,P}}_{=1} = S \tag{6}$$

Combining all terms:

$$\left(\frac{\partial T}{\partial N_j}\right)_{\underline{S},\,P,\,N_{i[j]}} = -\frac{ST}{NC_P} \tag{7}$$

What does this mean? T, N, and C_P are all positive, absolute numbers. But S, the molar entropy of the system, is only accurate to an arbitrary constant: its value depends on some reference state. Therefore, it could be a positive or negative number at the process conditions of interest. Since $d\underline{S} = (\delta Q/T)_{rev}$ we know that the value of S relates to heat flow in some way. Therefore, we conclude that depending on the reference state we choose for S, $(\partial T/\partial N_j)_{\underline{S},\,P,\,N_{i[j]}}$ can be positive *or* negative, and this reference state will determine if we need to add or remove heat from the system to keep $\underline{S}$ constant during the process.

To demonstrate, imagine that we start the experiment with the conditions in the cylinder exactly the same as the conditions of the incoming gas (320 K, 100 bar, etc.). Then, these states have the same molar entropy. Next, we pick a reference state such that the molar entropy is positive, so that $\underline{S}$ = constant > 0 always and $(\partial T/\partial N_j)_{\underline{S},\,P,\,N_{i[j]}} < 0$, or the temperature of the system must decrease . Now we start the experiment. Since the incoming CO_2 carries entropy with it, to keep entropy constant we must remove heat, hence the temperature drops.

Now we repeat the experiment, except this time we chose a reference state such that the molar entropy is negative, so that $\underline{S}$ = constant < 0 always and $(\partial T/\partial N_j)_{\underline{S},\,P,\,N_{i[j]}} > 0$. When we start the experiment, the incoming CO_2 carries entropy in with it. However, since the molar entropy of the CO_2 is the same as that of the initial state of the gas in the cylinder, it also has a negative molar entropy, so the entropy it carries with it has a negative value, thus decreasing the value of $\underline{S}$ of the system. To keep $\underline{S}$ constant, we must increase the entropy by heating the system, hence the temperature increases. This demonstrates how reference state dictates experimental procedure.