**10.40 Thermodynamics** **Fall 2003**

**Problem Set 6**

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Problem 1

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Consider a gas mixture of carbon dioxide and nitrogen at 298 K and 5 bar.

(a) How would you model this mixture in terms of its enthalpy and entropy? Be sure to specify your reference states when describing your model.

(b) Estimate the minimum work required to separate 100 moles of a 40 mole% nitrogen mixture into pure carbon dioxide and nitrogen.

(c) Would your model need to change if the pressure were increased to 200 bar? If so, how? You are not required to perform detailed calculations, but be sure to give your approach to solving the problem. Include any parameters that you would need to look up or estimate in order to solve the problem.

**Solution:**

(a)

Since the pressure is relatively low, it should be reasonable to model this mixture as a mixture of ideal gases. We can check this assumption by calculating the reduced temperature and pressure for each component and using Fig. 8.3 to determine how close the compressibility, Z, is to zero. The table below shows the relevant information. As we can see, the compressibility for each is very close to 1, so that an ideal gas assumption is justified.

| **Species** | **$T_c$ (K)** | **$T_r$** | **$P_c$ (bar)** | **$P_r$** | **Z** |
|---|---|---|---|---|---|
| $CO_2$ | 304.2 | 0.98 | 73.8 | 0.068 | ~0.99 |
| $N_2$ | 126.2 | 2.36 | 33.9 | 0.147 | ~1.0 |

With the ideal gas assumption, we can now use as our equation of state

$$P\underline{V} = NRT \tag{1}$$

where $N$ = total number of moles in the system. To complete our model, we must pick reference states and determine how to model mixtures. The most common reference state is to define the reference state for each compound relative to its constitutive elements in appropriate stoichiometric ratios at $T$ = 298 K and $P$ = 1 bar. At these conditions, the enthalpy and entropy of pure elements is assumed to be zero. Therefore, $H^o_{N2} = 0$ and $S^o_{N2} = 0$, while $H^o_{CO2} = \Delta H^o_{f,CO2}$ and $S^o_{CO2} = \Delta S^o_{f,CO2}$. Since the enthalpy of an ideal gas is only a function of temperature:

$$H_i = H_i\left(T\right) = H_i^o + \int_{T^o}^{T} C_{p,i}\left(T\right)dT \tag{2}$$

Likewise, it can be seen from Equation (8-23) that for an ideal gas:

$$S_i = S_i\left(T,P\right) = S_i^o + \int_{T^o}^{T} \frac{C_{p,i}\left(T\right)}{T}\,dT - \int_{P^o}^{P} \frac{R}{P}\,dP \tag{3}$$

With the pure component models done, we must now determine how to model the mixtures. To do this, we will follow the method outlined in Section 9.6 of T&M for ideal solutions. Since the enthalpy of an ideal gas mixture is only a function of temperature, and not composition, then it is evident that $\Delta H^{igm}{}_{mix} = 0$, and from Equation (9-99) we conclude that:

$$H^{igm} = \sum_{i=1}^{n} y_i H_i \tag{4}$$

To determine $S^{igm}$, we start with Equation (9-69) for the Gibbs Free Energy:

$$\Delta G_{mix}^{igm} = G^{igm}\left(T,P,y_1,\ldots,y_{n-1}\right) - \sum_{i=1}^{n} y_i G_i^o\left(T,P,y_i = 1\right) \tag{5}$$

Note that we have taken as a reference state the pure component species *i* at the same *T*, *P*, and state of aggregation as the mixture. This differs from the reference state used to determine *H* and *S* of the pure components in that the *T* and *P* of those reference states are fixed at 298 K and 1 bar, respectively, and that the reference state is relative to the constitutive elements of the components, not the components themselves. Next, we note that from Equation (9-10)

$$G^{igm} = \sum_{i=1}^{n} y_i \bar{G}_i$$

Also, from Equations (9-81) and (9-82), for an ideal gas mixture:

$$\begin{aligned} \bar{G}_i &= RT\ \ln p_i + \lambda_i\left(T\right) \\ &= RT\left(\ln P + \ln y_i\right) + \lambda_i\left(T\right) \end{aligned} \tag{6}$$

$$G_i^o = RT\ \ln P + \lambda_i\left(T\right) \tag{7}$$

Combining Eqns. (5), (6), and (7), we see that:

$$\Delta G_{mix}^{igm} = \sum_{i=1}^{n} y_i \left[ RT\left(\cancel{\ln P} + \ln y_i\right) + \cancel{\lambda_i\left(T\right)} \right] - \sum_{i=1}^{n} y_i \left[ \cancel{RT\ \ln P} + \cancel{\lambda_i\left(T\right)} \right] \tag{8}$$

$$\Delta G_{mix}^{igm} = RT\sum_{i=1}^{n} y_i\ \ln y_i \tag{9}$$

Noting that $\Delta G_{mix} = \Delta H_{mix} - T\,\Delta S_{mix}$, and applying Equation (9-99) again:

$$\Delta S_{mix}^{igm} = -R\sum_{i=1}^{n} y_i\ \ln y_i \tag{10}$$

$$S^{igm} = \sum_{i=1}^{n} y_i S_i - R\sum_{i=1}^{n} y_i\ \ln y_i \tag{11}$$

This gives us all the equations we need to model the $CO_2$-$N_2$ mixture. Note that the mixing functions are the same as those for an ideal solution. However, an ideal gas mixture and an ideal solution are not identical, since for an ideal gas mixture $PV=RT$. This is not necessarily true for an ideal solution.

(b)

The solution to this problem is discussed extensively in Section 9.9 of Tester & Modell and in Example 9.8. It can be done by either finding the change in availability for the process or by calculating $\Delta \underline{G}_{mix}$ for the solution. We can use the mixing functions for an ideal gas mixture derived in part (a). Since we are going from mixed to unmixed at constant temperature:

$$W_{min} = \Delta \underline{B} = N\Delta B = -N\left(\underbrace{\Delta H_{mix}^{igm}}_{=0} - T_O \Delta S_{mix}^{igm}\right) = -N\Delta G_{mix}^{igm} \tag{12}$$

$$\begin{aligned} W_{min} &= N\left(T_O R \sum_{i=1}^{n} y_i \ln y_i\right) \\ &= (1000 \text{ moles})\left[298 \text{ K } 8.314 \ \frac{\text{J}}{\text{mol K}}\left(0.4 \ln 0.4 + 0.6 \ln 0.6\right)\right] \end{aligned} \tag{13}$$

$$W_{min} = 166700 \text{ J or } 166.7 \text{ kJ}$$

(c)

At a pressure of 200 bar, we are no longer going to be able to model these gases as an ideal gas mixture and would have to use some other, more accurate, equation of state. For example, the Redlich-Kwong-Soave or Peng-Robinson EOS may be appropriate. Any model would have to be checked against actual data to ensure an adequate fit. In addition to the normal parameters needed for these equations of state, such as critical constants, mixing rules will have to be chosen. Some commonly chosen mixting rules are those proposed by Lorentz and Berthelot:

$$b_m = \sum_{i=1}^{n} x_i b_i \qquad a_m = \left[\sum_{i=1}^{n} x_i \left(a_i\right)^{1/2}\right]^2$$

where $b_i$ and $a_i$ are the parameters used in the RKS and PR EOS's for pure single components. Another popular approach for the case where the components have very dissimilar molecular properties and the above mixing rules do not give a good fit is to include "binary interaction parameters" that are fit to data to give a better fit. For example, $b_m$ may be used as above, but $a_m$ is modified to include the interaction parameter $\delta_{ij}$, where:

$$a_m = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = \left(1 - \delta_{ij}\right)\sqrt{a_i a_j} \quad i \neq j$$

$$a_{ii} = a_i \quad a_{jj} = a_j$$

$$\delta_{ii} = \delta_{jj} = 0$$

The greater the interaction between components $i$ and $j$, the larger the value of $\delta_{ij}$. Using such an EOS, the model is then built in a method similar to that shown in part (a). Specifically, we could assume the same pure component reference state as before, and applying Equations (9-69), (9-107), (9-82) and (9-120) we get:

$$\Delta G_{mix} = \sum_{i=1}^{n} y_i \left[ \overline{G}_i - G_i \right] = RT \sum_{i=1}^{n} y_i \ln \hat{\phi}_i \tag{14}$$

The fugacity coefficient can be calculated using Eq. (9-129) or Eq. (9-142).