

1. Calculate the molar free energy of mixing of a salt solution of 0.1 M sodium carbonate and 0.1 M magnesium carbonate at 300 K.

Solution: 0.1 M  $\text{Na}_2\text{CO}_3$  gives 0.2 mole of  $\text{Na}^+$  and 0.1 mole  $\text{CO}_3^{2-}$  ions per liter. 0.1 M  $\text{MgCO}_3$  gives 0.1 mole of  $\text{Mg}^{2+}$  and 0.1 moles of  $\text{CO}_3^{2-}$  ions per liter. There is no entropy of mixing for the  $\text{CO}_3^{2-}$  ions. However, there is an entropy of mixing for the cations,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . We need to determine the mole fractions and then plug the mole fractions into the expression for the molar free energy.

$$x_{\text{Na}} = \frac{n_{\text{Na}}}{n_{\text{Na}} + n_{\text{Mg}}} = \frac{0.2}{0.2 + 0.1} = \frac{2}{3}$$

$$x_{\text{Mg}} = \frac{n_{\text{Mg}}}{n_{\text{Na}} + n_{\text{Mg}}} = \frac{0.1}{0.2 + 0.1} = \frac{1}{3}$$

$$\begin{aligned} \Delta S_m &= -R(x_{\text{Na}} \ln x_{\text{Na}} + x_{\text{Mg}} \ln x_{\text{Mg}}) \\ &= -8.31 \text{ J/mol-K} (0.1 \ln (0.1) + 0.2 \ln (0.2)) \\ &= 4.59 \text{ J/mol-K} \end{aligned}$$

$$\begin{aligned} \Delta G_m &= -T\Delta S_m = RT(x_{\text{Na}} \ln x_{\text{Na}} + x_{\text{Mg}} \ln x_{\text{Mg}}) \\ &= -(8.31 \text{ J/mol-K})(300 \text{ K})(0.1 \ln (0.1) + 0.2 \ln (0.2)) \\ &= 1376.5 \text{ J/mol} \end{aligned}$$

2. In class we calculated the value of the pressure for which diamond is in equilibrium with graphite. Suppose that you are working for a company that wants to make diamond and they determine that they need a chemical potential of -80 kJ/mol for the reaction. What pressure does this correspond to?

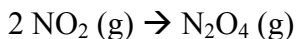
Solution: The difference here is that we must use the full relationship including DG (since  $\Delta G$  is not zero here!). We do the same thing we did in class. We solve for the pressure.

$$\begin{aligned} \Delta G &= \Delta G^0 + \Delta V_m(P - 1) \\ P &= 1 + \frac{\Delta G - \Delta G^0}{\Delta V_m} = 1 + \frac{\Delta G - \Delta G^0}{\frac{M}{\rho_d} - \frac{M}{\rho_{gr}}} \end{aligned}$$

$$= 1 + \frac{-80000 \text{ J/mol} - 2900 \text{ J/mol}}{0.012 \text{ kg/mol} \left( \frac{1}{3510} - \frac{1}{2260} \right)}$$

$$= 4.4 \times 10^{10} \text{ Pa} = 440 \text{ kilobars}$$

3. Consider the reaction:



The reaction takes place in a closed container at constant pressure. If the initial pressures are  $P_{\text{NO}_2} = 1 \text{ atm}$ , what is the pressure of  $\text{N}_2\text{O}_4$  at equilibrium?

a. Construct a table to determine the partial pressure of the gases at equilibrium in terms of the extent of reaction,  $x$ .

Solution:

Condition	$\text{NO}_2$	$\text{N}_2\text{O}_4$	Total
Initial pressure	1	0	0
Equilibrium moles	$1 - 2x$	$x$	$1 - x$

b. Use free energy values to determine the magnitude of the equilibrium constant.

$$K = \exp\{4730/8.31/298\} = 6.75$$

c. Determine the relationship between the extent of reaction,  $x$  and the equilibrium constant.

$$K = \frac{x}{(1 - 2x)^2}, \quad K - (4K + 1)x + 4Kx^2 = 0$$

$$x = \frac{4K + 1 \pm \sqrt{16K^2 + 8K + 1 - 16K^2}}{8K}$$

$$x = \frac{4K + 1 \pm \sqrt{8K + 1}}{8K}$$

d. Calculate the extent of reaction,  $x$ .

Substituting in the numbers we find  $x = 0.381$ .