Chemistry 410B **Exam 6** **Spring 2008**

Solutions

1. Consider the osmotic cell-within-a-cell design sketched below. The membrane between 1 and 2 is permeable only to solvent A, and the membrane between 2 and 3 is permeable to both A and B but not C. Find an expression for the *total pressure* P_3 in terms of P_1 and the molarities [B] and [C] in cell 3. Assume that X_{A} is much greater than X_{B} and X_{C}. **Solution:** The way we solved the problem for the single-cell case was by setting the chemical potentials of the solvent A equal in each region. So let's skip the second region and just equate μ_{A} in regions 1 and 3:

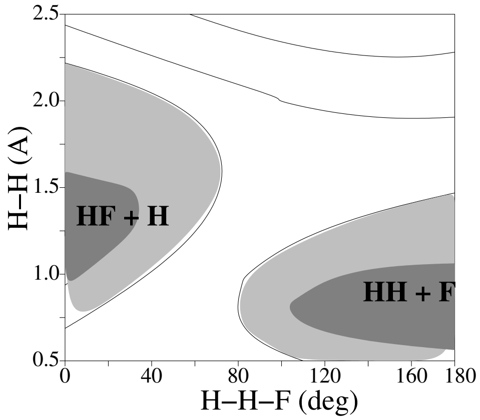
$$\begin{aligned}
\mu_{\mathrm{A1}} &= \mu_{\mathrm{A3}} \\
\mu^\bullet_{\mathrm{A}}(P^\ominus) + V_{m\mathrm{A}}(P_1 - P^\ominus) &= \mu^\bullet_{\mathrm{A}}(P^\ominus) + V_{m\mathrm{A}}(P_3 - P^\ominus) + RT\ln a_{\mathrm{A}} \\
V_{m\mathrm{A}}(P_1 - P_3) &= RT\ln a_{\mathrm{A}} \approx RT\ln X_{\mathrm{A}} = RT\ln(1 - X_{\mathrm{B}} - X_{\mathrm{C}}) \\
&\approx -RT(X_{\mathrm{B}} + X_{\mathrm{C}}) \\
P_3 &\approx P_1 + \frac{RT(X_{\mathrm{B}} + X_{\mathrm{C}})}{V_{m\mathrm{A}}} = P_1 + RT([\mathrm{B}] + [\mathrm{C}])
\end{aligned}$$

2. Find an equation for the slope phase boundary of a two-component liquid as it approaches the eutectic point on a T vs. X phase diagram. **Solution:** In arriving at the equation for freezing point depression, we needed the derivative of $\ln a_{\mathrm{A}}$ with respect to T, and this in turn is related to the concentration X_{B}:

$$\begin{aligned}
\frac{\partial \ln a_{\mathrm{A}}}{\partial T} &= \frac{\Delta_{\mathrm{fus}} H^\bullet_{\mathrm{A}m}}{RT^2} \\
&\approx \frac{\partial(1 - X_{\mathrm{B}})}{\partial T} = -\frac{\partial X_B}{\partial T} \\
\frac{\partial T}{\partial X_{\mathrm{B}}} &\approx -\frac{RT^2}{\Delta_{\mathrm{fus}} H^\bullet_{\mathrm{A}m}}
\end{aligned}$$

So the phase boundary is correctly predicted to be a curve of increasingly negative slope as it approaches the discontinuity at the eutectic.

3. Sketch the contours to complete a **qualitative** version of the $H_2 + F$ reaction surface as a function of the H-H distance and the **H-H-F angle**.



4. A sample of 0.500 mol H_2S gas reacts with O_2 gas completely to yield H_2O and SO_3, both in the gas phase. If the reactants start at 298 K and the final temperature is 458 K, what is the total change in entropy for this sample? **Solution:** Model this as a two step process: the first step is the isothermal reaction at 298 K; the second is heating the products to the final temperature of 458 K. The reaction is

$$H_2S(g) + 2O_2(g) \longrightarrow H_2O(g) + SO_3(g)$$

And don't forget in the final answer that the amount of material was specified:

$$\begin{aligned}\Delta_{\text{rxn}}S &= \Delta_{\text{rxn}}S(298\text{ K}) + C_P(\text{prod}) \ln\frac{458}{298} \\ &= \left\{[188.825 + 256.76 - (205.79 + 2\cdot 205.138)] + (33.577 + 50.67)\ln\frac{458}{298}\right\}(\text{ J K}^{-1}\text{ mol}^{-1}) \\ &= (-170.481 + 36.207)(\text{ J K}^{-1}\text{ mol}^{-1}) = -67.14\text{ J K}^{-1}\text{ mol}^{-1}\end{aligned}$$

and multiply by the actual amount 0.500 mol of H_2S initially to get $\Delta S = \boxed{-62.14\text{ J K}^{-1}}$.

5. Identify the number of degrees of freedom for each reactant and product in the two following reactions, and indicate whether the overall $\Delta_{\text{rxn}}S$ is likely to be positive or negative:

			$2O_2(g)$	$\longrightarrow$	$O_3(g)$	+	$O(g)$
translational			$2\cdot 3 = 6$		3		3
rotational			$2\cdot 2 = 4$		3		0
vibrational			$2\cdot 1 = 2$		3		0
$\Delta_{\text{rxn}}S$ + or −	$\boxed{-}$						
	$GeH_4(g)$	+	$2O_2(g)$	$\longrightarrow$	$GeO_2(s)$	+	$2H_2O(g)$
translational	3		$2\cdot 3 = 6$		0		$2\cdot 3 = 6$
rotational	3		$2\cdot 2 = 4$		0		$2\cdot 3 = 6$
vibrational	9		$2\cdot 1 = 2$		9		$2\cdot 3 = 6$
$\Delta_{\text{rxn}}S$ + or −	$\boxed{-}$						