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 $\mu_A$ in regions 1 and 3:

$$\mu_{A1} = \mu_{A3}$$

$$\mu^*(P^*) + V_{mA}(P_1 - P^*) = \mu^*(P^*) + V_{mA}(P_3 - P^*) + RT \ln a_A$$

$$V_{mA}(P_1 - P_3) = RT \ln a_A \approx RT \ln X_A = RT \ln(1 - X_B - X_C)$$

$$P_3 \approx P_1 + \frac{RT(X_B + X_C)}{V_{mA}} = P_1 + RT([B] + [C])$$

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 $\ln a_A$ with respect to $T$, and this in turn is related to the concentration $X_B$:

$$\frac{\partial \ln a_A}{\partial T} = \frac{\Delta_{fus}H^{\bullet}_{Am}}{RT^2}$$

$$\approx \frac{\partial (1 - X_B)}{\partial T} = -\frac{\partial X_B}{\partial T}$$

$$\frac{\partial T}{\partial X_B} \approx -\frac{RT^2}{\Delta_{fus}H^{\bullet}_{Am}}$$

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 $\text{H}_2 + \text{F}$ reaction surface as a function of the H-H distance and the $\text{H-H-F}$ angle.
4. A sample of 0.500 mol H₂S gas reacts with O₂ gas completely to yield H₂O and SO₃, 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

\[
\text{H}_2\text{S}(g) + 2\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(g) + \text{SO}_3(g)
\]

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

\[
\Delta_{\text{rxn}}S = \Delta_{\text{rxn}}S(298 \text{ K}) + C_P(\text{prod}) \ln \frac{458}{298}
\]

\[
= \left\{ \left[188.825 + 256.76 - (205.79 + 2 \cdot 205.138)\right] + (33.577 + 50.67) \ln \frac{458}{298} \right\} (\text{ J K}^{-1} \text{ mol}^{-1})
\]

\[
= (-170.481 + 36.207)(\text{ J K}^{-1} \text{ mol}^{-1}) = -67.14 \text{ J K}^{-1} \text{ mol}^{-1}
\]

and multiply by the actual amount 0.500 mol of H₂S initially to get \(\Delta S = -62.14 \text{ J K}^{-1}\).

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:

<table>
<thead>
<tr>
<th></th>
<th>(2\text{O}_2(g) \longrightarrow \text{O}_3(g) + \text{O}(g))</th>
<th>(\text{GeH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{GeO}_2(s) + 2\text{H}_2\text{O}(g))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>translational</strong></td>
<td>2 \cdot 3 = 6</td>
<td>2 \cdot 3 = 6</td>
</tr>
<tr>
<td><strong>rotational</strong></td>
<td>2 \cdot 2 = 4</td>
<td>2 \cdot 2 = 4</td>
</tr>
<tr>
<td><strong>vibrational</strong></td>
<td>2 \cdot 1 = 2</td>
<td>2 \cdot 1 = 2</td>
</tr>
<tr>
<td>(\Delta_{\text{rxn}}S) + or −</td>
<td>−</td>
<td>−</td>
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</tbody>
</table>